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DYNAMICAL THEORY OF ALBUMINOID AMMONIA.[1]

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The following investigation was suggested by committee work of the American Association for the Advancement of Science, on water analysis. It is an attempt to apply well established principles of mass action to certain questions involved in the determination of albuminoid ammonia. The following points have been kept in view:

1. Can some probable correction be made for the error incurred by stopping the distillation while ammonia is still coming off?
2. What modification of the original method seems rational?
3. What insight can be gained into the nature of the chemical process?

The experimental basis of the following paper will be found in Mallet's report on the determination of organic matter in potable water,[2] with the addition of some details kindly communicated by Dr. Charles Smart.

I. *Distillation of Free Ammonia.*

In the distillation of albuminoid ammonia, two stages must be distinguished: first, oxidation of the nitrogenous body by the alkaline solution of permanganate; and, second, the separation of

[1] Prepared for the Toronto meeting of the American Association for the Advancement of Science.

[2] Report of the National Board of Health for 1889.

ammonia thus formed by distillation. It will be most convenient to begin with the discussion of this second process, which is essentially physical. As in any other case of fractional distillation, water and ammonia both pass from the fluid to the gaseous or vapor condition, in accordance with their respective tensions and mass.

Let x = volume of fluid in retort,
y = weight of ammonia in retort,
z = weight of ammonia in distillate.

Then $\frac{y}{x}$ = concentration of fluid in retort,

$\frac{dy}{dx} = \frac{-dz}{dx}$ = concentration of any small portion of distillate.

The coefficient of volatility may be defined as the ratio of the concentration in any small portion of distillate to that of the fluid in retort. Designating this coefficient as k,

$$\frac{dy}{dx} = k \cdot \frac{y}{x}. \qquad (1)$$

In the ordinary distillation of ammonia, k is found to be approximately constant, and it will be so regarded here. By integration,

$$\log_e y = k \cdot \log_e x + \text{constant};$$

using zero subscript to denote initial conditions,

$$\log_e y_0 = k \cdot \log_e x_0 + \text{constant},$$

$$\therefore \quad \log_e \frac{y}{y_0} = k \cdot \log_e \frac{x}{x_0},$$

or

$$\log \frac{y}{y_0} = k \cdot \log \frac{x}{x_0}, \qquad (2)$$

a very useful formula for determining the coefficient of volatility and tracing the progress of distillation. Curve A, in the figure, represents y as that function of x defined by equation (2).

Wanklyn,[1] who was the first to use and define the term coefficient of volatility, reports four experiments for its determination. One liter of dilute aqueous ammonia was distilled in each case until 50 cc. of distillate had been collected. As nearly one-half the ammonia taken was distilled with the first 5 per cent. of water (the concentration in the retort being gradually reduced at the same

[1] Phil. Mag. [4], **45**, 132 (Feb. 1873).

time), Wanklyn estimated k equal to "about thirteen or fourteen." The experimental data are given below with more precise values of k, as calculated by equation (2). In each case, $x_0 = 1000$, $x = 950$. The quantities of ammonia taken, and that found in the distillate, are expressed in milligrams under y_0 and z respectively; the difference (remaining in retort) under y:

y_0.	z.	y.	k.
1000	480	520	12.74
1	.50	.50	13.50
.5	.235	.265	12.39
.2	.095	.105	12.55

Mean = 12.8

This value may be rather too low, as no account is taken of a possible loss from imperfect condensation, a loss averaging 7.2 per cent. in Smart's experiments.

The same author observes also[1] that in the distillation of one-half liter of water, the ammonia found in the first measure of 50 cc. is three-fourths of the whole quantity of ammonia obtained. By equation (2), assuming that any loss affects each part in the same proportion,

$$\log \tfrac{1}{4} = k \,.\, \log \tfrac{9}{10},$$

$$\therefore \quad k = 13.14.$$

Thirty experiments by Smart to determine the loss of ammonia by imperfect condensation are also available for the estimation of k, the successive measures of distillate having been nesslerised separately.[2] A single distillation affords several values, as each fraction determined may be compared with the whole quantity found in subsequent fractions. The values thus deduced vary from 10 to 16, with a few instances beyond these extremes. The variations in the values of k do not show any well marked relation to the whole quantity of ammonia present, to the amount of loss, nor to the rate of boiling. The experimental work was done wholly for another purpose, and probably with just such care as the conscientious analyst would ordinarily give. We may then assume 13 as a mean value for k, remembering that considerable allowance must be made for unexplained variations.

[1] Wanklyn's *Water Analysis*, 6th and 7th editions, p. 41.

[2] Most of these data appear in the Report of the National Board of Health for 1882, pages 312-314.

II. *Application of Formula to Estimation of Free Ammonia.*

In the analytical process it is usual to distill three or four fractions, each nearly equal to one-tenth of the original volume. For 100 parts of free ammonia present, when $k = 13$, theory would lead us to expect, in four successive fractions, the increments named below under Δz, with loss of 0.13; vertical lines in the figure, a, a, a, represent these increments geometrically. The ratio of each increment to the next is stated under r. The mean values of the ratios obtained in the experiments to determine loss of ammonia are given under r':

No.	Δz.	r.	r'.
1	74.6	3.75	4.23
2	19.9	4.4	5.26
3	4.53	5.4	5.65
4	.84		

In the analyses of natural waters reported (*loc. cit.* pp. 321–330), considerable variation appears in the ratios of successive increments, but usually not more than might be expected from the observed variations in k. Analyses No. 18 and No. 54 are exceptional and happen to give identical results, the free ammonia being .015, .01, and .01 mgm. in the three fractions nesslerised, with ratios 1.5 and 1. In such cases there is a strong probability that some more complex body is gradually decomposed by simple boiling with sodium carbonate. Small ratios between the successive fractions of "free ammonia" may lead to suspicion of urea contamination, though of course due caution should be used in drawing such conclusions. The analyst will at least find it instructive to enter the ratios in his note-book, together with the separate results of nesslerising; this will appear more plainly in the following sections. The slowness of the chemical action usually retards the distillation of albuminoid ammonia, giving rise to much smaller ratios between successive fractions than those named above.

III. *Action of Mass in Formation of Albuminoid Ammonia.*

We must now attempt to follow the chemical as well as the physical aspect of the process. In the former the reactions may be much involved, and various formulas may be required to represent the successive formation and destruction of different substances. Let us consider, as an ideal case, a single chemical

reaction, involving one molecule each of three reacting bodies; the formation of ammonia taking place at each moment of distillation, in each cubic centimeter of the fluid, in proportion to the product of the quantities of the nitrogenous body, the potash, and the permanganate present therein.

Retaining the use of x, y, and z as explained in section I, let

u = weight of the nitrogenous body in the retort,

v = weight of potash in the retort,

w = weight of potassium permanganate in the retort,

t = time, in minutes, from the beginning of the reaction,

a = coefficient of speed.

Assume also a uniform rate of distillation, in which

b = volume distilled per minute,

bc = volume of fluid in retort at the beginning of the action; whence

$$x = bc - bt,$$

and

$$dx = -bdt.$$

Then $\frac{u}{x}$, $\frac{v}{x}$, and $\frac{w}{x}$ = weights of the three active substances in each cubic centimeter of fluid in the retort,

$$-\frac{du}{dt} = b\,\frac{du}{dx} = \text{rate of change},$$

and, by the law of mass action,

$$b\,\frac{du}{dx} = a\,.\,\frac{u}{x}\,.\,\frac{v}{x}\,.\,\frac{w}{x}\,.\,x = avw\,.\,\frac{u}{x^3},$$

$$\therefore\quad \frac{du}{u} = \frac{avw}{b}\,.\,\frac{dx}{x^3}. \qquad (3)$$

The reagents are present in such large excess that v and w may be regarded as constants (unless the permanganate suffers from an unusual amount of pollution), and by integration,

$$\log_e u = -\frac{avw}{b}\,.\,\frac{1}{x} + \text{constant},$$

$$\log_e u_0 = -\frac{avw}{b}\,.\,\frac{1}{x_0} + \text{constant},$$

$$\therefore\quad \log_e \frac{u}{u_0} = -\frac{avw}{b}\,.\,\frac{x_0 - x}{x_0 x},$$

which may be written

$$-\log \frac{u}{u_0} = \frac{avw}{bx_0 \log_e 10}\,.\,\frac{x_0 - x}{x} = A\,.\,\frac{x_0 - x}{x}. \qquad (4)$$

This equation represents any one reaction of the kind specified during the concentration required in an ordinary estimation of albuminoid ammonia, but the mathematical expression must not be pressed too far. Thus, if we make $x = 0$, this not only implies that the contents of the retort are evaporated to dryness, but also that the reagents have gained infinite concentration, and therefore act with resistless force, effecting complete alteration of any remaining traces of the nitrogenous body. The form of the curve varies greatly with the value of A. Two examples are given in the figure. Curve B represents this equation when $A = 1$; curve C when $A = \frac{1}{10}$. Since the quantity of ammonia present at any moment (both in retort and distillate) is proportional to the weight of the nitrogenous body transformed, we may write

$$u_0 - u : u_0 :: (y + z) : (y + z)_\infty,$$

where subscript ∞ is used to denote the ultimate value theoretically possible; or, in another form (since $y_\infty = 0$),

$$\frac{u}{u_0} = \frac{z_\infty - (y + z)}{z_\infty}. \qquad (5)$$

The curves B and C are so drawn that ordinates represent $(y + z)$ as a function of x.

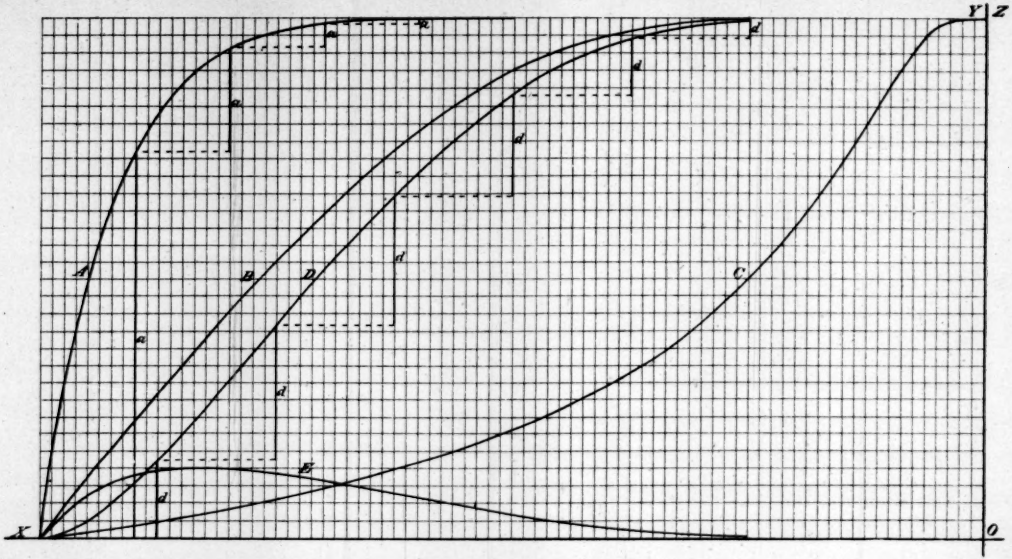
It will be seen at once that when $A = 1$ the quantity of ammonia increases very rapidly during the first part of the distillation, but when $A = 0.1$, $(y + z)$ increases but slowly until the fluid is considerably concentrated. Equation (4) suggests various modifications by which A may be altered at pleasure; for example, by increasing the quantity of permanganate used (represented by w), or by distilling a less quantity (b) each minute. Thus Smart noted several instances of increased action by slower boiling.

Curves of similar properties express the progress of other reactions which take place during concentration in large excess of reagents. Equations of the following forms are obtained by varying the exponent of x in equation (3) and using the appropriate constants. For reactions involving the concurrence of two molecules only,

$$-\log \frac{z_\infty - (y + z)}{z_\infty} = -A \cdot \log \frac{x}{x_0}. \qquad (6)$$

For three molecules,

$$-\log \frac{z_\infty - (y + z)}{z_\infty} = A \frac{x_0 - x}{x}. \qquad (7)$$



EXPLANATION OF THE FIGURE.

A. Curve of distillation of free ammonia. a, a, a. Fractions, each $\frac{1}{10}$ the original volume. *B*. Formation of albuminoid ammonia, eq. (7); $A=1$. *C*. Formation of albuminoid ammonia, eq. (7), $A=\frac{1}{10}$. *D*. Ammonia in distillate, from curve *B*. d, d, d. Fractions, each $\frac{1}{4}$ the original volume. *E*. Ammonia in retort, from curve *B*. Values of x, although positive, are measured towards the *left*, in order that time may be counted towards the *right*.

For four molecules,

$$-\log \frac{z_\infty - (y+z)}{z_\infty} = A \frac{x_0^2 - x^2}{x^2}. \qquad (8)$$

In all such cases the formation of ammonia may take place most rapidly in the early, middle or latter part of the distillation, according to the value of A.

If the ammonia, instead of appearing directly, is the final product of a succession of different reactions, a complete theory must take account of the gradual formation and disappearance of the intermediate products. Some evidence on this point will appear in section VI.

IV. *Distillation of Albuminoid Ammonia.*

Equation (1) applies to the distillation of ammonia only when the total quantity $(y+z)$ remains constant; otherwise we must write $-dz$ in place of dy. Thus,

$$\frac{-dz}{dx} = k \cdot \frac{y}{x}, \qquad (9)$$

or

$$y = -\frac{x}{k} \cdot \frac{dz}{dx}. \qquad (10)$$

Substituting in equation (7),

$$-\log \left(1 + \frac{x dz}{k z_\infty dx} - \frac{z}{z_\infty}\right) = A \frac{x_0 - x}{x}. \qquad (11)$$

This equation (as soon as a fixed value is given to A) expresses a perfectly definite relation between the ammonia distilled and the volume remaining in the retort. It is not easy, however, to obtain an integral in form suitable for computation, and an indirect method was used. The ordinates of curve B represent the sum of y and z when $A = 1$; these ordinates were divided into two parts, in accordance with the condition implied in equation (9). Curve D thus represents the gradual increase of z, and curve E shows the increase and subsequent decrease of y. A few corresponding points of these three curves are also indicated in the following table, increments of z being placed under the symbol Δz. These increments are shown on the figure as d, d, d. For convenience, z_∞ is taken as unit of weight for ammonia, and x_0 is made equal to 8; as when a volume of 400 cc. is distilled in fractions of 50 cc. each. The ratio of each increment to the next is stated under r.

x.	$y+z$.	y.	z.	Δz.	r.
8	.000	.000	.000	...	...
7	.280	.129	.151	.151	.58
6	.535	.122	.413	.262	1.05
5	.749	.087	.662	.249	1.31
4	.900	.047	.853	.191	1.74
3	.978	.015	.963	.110	3.23
2	.999	.002	.997	.034	...
0	1.000	.000	1.000	...	...

When $A=1$ (as in this table), y reaches a maximum when $x=6.7$, during the collection of the second fraction of distillate; and this fraction contains the largest quantity of ammonia. The third fraction contains nearly the same amount, but later increments show a rapid decrease. The large increase of ammonia indicated for the second measure is due in very small part to the increased concentration of the permanganate, but chiefly to the fact that sufficient time has elapsed for the accumulation of ammonia in the retort. An increase in the second measure has been rarely observed in practice, except in a few experiments on pure chemicals, such as urea, theine, glychocholic acid, and notably in cyanuric acid. In the 59 samples of natural waters already referred to, the first measure always contained as much as $1\frac{1}{2}$ times that found in the second; in 11 instances the ratio is 2, and in 33 instances it is more than 2. On the other hand, instead of an increase in this ratio for succeeding portions (as indicated by theory for a single reaction), it usually decreases, the ratio of the last two determinations being from 1 to 2. This want of agreement between the theory for a single reaction and observations on a natural water are exactly what we should expect; for the water may contain a great number of different substances, each undergoing change according to equation (6), (7) or (8), so that the actual rate of distillation depends upon the sum of the ammonia derived from all these sources. As curve E shows a rapid rise from zero to a maximum, followed by a gradual decrease to zero, so we may conceive a multitude of similar curves, with their several maxima at various points, but with a large share of them near the origin; implying $A>1$, for the most part. The resultant of all such curves might have a single maximum, like the type given, or it might have a succession of maxima and minima. On the theory of averages,

the former seems more probable. This resultant curve might have a great variety of form in details, answering to the various behavior of different waters.

V. *Exterpolation Formula for Residue in Retort.*

Many chemists, feeling that the task is not completed by nesslerising three measures, have pushed the distillation much farther. Mallet[1] suggests a certain limit as criterion when the distillation has been carried far enough. If the ammonia found in the successive portions is reported, we can rudely plat the curves for ammonia distilled, ammonia in retort, or total ammonia formed. Each of these curves may be the resultant of many similar curves having different parameters. Can we find an empirical equation for the resultant that will conform to the analytical results, and thus enable us to apply a probable correction for the ammonia that would be obtained if the distillation were completed?

We may assume a curve of the form

$$y = Ax + Bx^2 \qquad (12)$$

to indicate the varying quantity of ammonia in the retort under the condition that this is all distilled away when the fluid is gone. Substituting in equation (9),

$$\frac{-dz}{dx} = kA + kBx.$$

Integrating between the limits z_1 and z_2,

$$z_2 - z_1 = kA(x_1 - x_2) + \tfrac{1}{2}kB(x_1^2 - x_2^2);$$

or, for brevity,

$$\Delta_1 z = kA\Delta_1 x + \tfrac{1}{2}kB\Delta_1 x^2. \qquad (13)$$

In like manner, for a second increment of z and for the undetermined portion,

$$\Delta_2 z = kA\Delta_2 x + \tfrac{1}{2}kB\Delta_2 x^2,$$
$$\Delta_\infty z = kA\Delta_\infty x + \tfrac{1}{2}kB\Delta_\infty x^2. \qquad (14)$$

Those who follow Wanklyn's directions for 500 cc. of water begin the distillation of albuminoid ammonia with 350 cc. of fluid, and distill three measures of 50 cc. each, rejecting the last 200 cc. Taking 50 cc. as unit of volume, $x_1 = 6$, $x_2 = 5$, and $x_3 = 4$, while $\Delta_1 z$ and $\Delta_2 z$ represent the ammonia found in the second and third measures. Assume $\Delta_1 z = r\Delta_2 z$, then

[1] *Loc. cit.* p. 208.

$$r\Delta_2 z = kA(6-5) + \tfrac{1}{2}kB(36-25) = kA + 5.5kB,$$
$$\Delta_2 z = kA(5-4) + \tfrac{1}{2}kB(25-16) = kA + 4.5kB.$$

By elimination,

$$kB = (r-1)\Delta_2 z \text{ and } kA = (5.5 - 4.5r)\Delta_2 z.$$

But
$$\Delta_\infty z = 4kA + 8kB,$$
$$\therefore \Delta_\infty z = (14 - 10r)\Delta_2 z. \qquad (15)$$

If $r = 1$, $\Delta_\infty z = 4\Delta_2 z$;

that is, if the second and third measures yield like quantities of ammonia, the best correction we can make is to assume that the distillation of four times 50 cc. still remaining in the retort would yield four times that quantity.

If $r > 1\frac{8}{10}$, the value of A becomes negative, and therefore y becomes negative for small values of x. This involves a physical impossibility, but we may meet the difficulty by treating the equation

$$y = Ax^2 + Bx^3 \qquad (16)$$

in the same manner as equation (13), whence

$$\Delta_\infty z = \frac{188 - 100r}{37}\Delta_2 z, \qquad (17)$$

a correction which again fails if $r > 1\frac{81}{100}$.[1]

We may test these formulas by means of Smart's experiments with pure chemicals; but, as he began the action with 400 cc. of fluid instead of 350, $\Delta_1 z$ and $\Delta_2 z$ represent his third and fourth fractions, with the advantage of greater distance from the beginning of the operation, where equation (12) is wholly inapplicable. The available data (for values of r between 1 and 1.5) are given in the following table, which states under

[1] To obtain a more general formula for the correction proposed, we may assume

$$y = Ax^n + Bx^{n+1}, \qquad (18)$$

whence, by the same treatment illustrated above,

$$\Delta_\infty z = \frac{(\Delta_1 x^{n+1} - r\Delta_2 x^{n+1})\Delta_\infty x^n - (\Delta_1 x^n - r\Delta_2 x^n)\Delta_\infty x^{n+1}}{\Delta_2 x^n \Delta_1 x^{n+1} - \Delta_1 x^n \Delta_2 x^{n+1}}\Delta_2 z, \qquad (19)$$

where A is positive or zero when

$$r \leq \frac{\Delta_1 x^{n+1}}{\Delta_2 x^{n+1}}. \qquad (20)$$

We may either make n the smallest integer consistent with the condition (20), or we may determine n by making the fraction equal to r. The function $\Delta_\infty z = \phi(r)$ will be a smooth curve in either case, consistent with the theory as developed above and with the analytical results.

A, per cent. ammonia found in the first four fractions;
B, per cent. ammonia found in "exhaustive experiments";
C, per cent. ammonia obtainable after the first four fractions; and
D, per cent. ammonia indicated by the exterpolation formulas.

	A.	B.	C.	D.
Silver and potassium cyanide,	2.25	[17.1]	14.85	2.4
Prussian blue,	.3	25.8	25.5	.2
Urea, from urine,	8.7	43.10	34.4	8.8
	8.65	...	34.45	6.6
Urea, from ammonium cyanate,	7.7	43.4	35.7	8.0
	7.5	...	35.9	8.0
Alloxan,	6.55	21.3	14.75	2.5
	6.6	...	14.7	2.4
Thiocarbanilide,	4.15	11.85	7.7	1.6
Thiocarbamide,	15.25	22.50	7.25	1.7
	15.0	...	7.5	1.6
Strychnine sulphate,	4.0	5.4	1.4	.4
	3.75	...	1.65	1.0
Codeine,	5.0	5.32	.32	.5

A glance at the last two columns shows that the ammonia actually obtainable after one-half the fluid had been distilled was many times the proposed correction. An explanation of this discrepancy will next be considered.

VI. *Evidence of Intermediate Compounds of Nitrogen.*

Making some allowance for the difference between equation (7) (which was selected for study) and equations (6) and (8), it is safe to conclude from the table in section IV, that if the action of alkaline permanganate upon a pure compound of nitrogen could be represented by any single chemical equation (no matter how complex), we should have reason to expect this change to take place with such speed that fully 70 per cent. of the theoretical yield of ammonia would be obtained by distilling one-half the fluid, or else with such slowness that the first measure would contain far less ammonia than the second. Published experiments with at least eight bodies[1] contradict both these conditions, and we are forced to believe that in the earlier stages some molecules of the original body yield ammonia with promptness, while others

[1] These are the first six named in the last table, besides parabanic acid and theine.

are converted into more stable forms and resist the action with great stubbornness. The nature of these intermediate products is not yet clear, except only that *a* (as defined in section III) is small, in their reaction with alkaline permanganate. Perhaps they may be chiefly condensation products. Alloxan, which yielded 4 per cent. ammonia in the first fraction (eighth) of distillate, and only 2.57 per cent. in the next three, but 21.3 per cent. by prolonged action, is a marked example of such behavior; this, no doubt, is partly converted into parabanic acid. So, likewise, in a water analysis, many substances may yield a small part of their nitrogen as ammonia, while the greater part is converted into more stable forms which elude detection. It has been supposed that the organic matter of potable water is more like asparagine, yielding its nitrogen readily under the action of permanganate. Of this, however, I have found no proof. In about 40 per cent. of the natural potable waters referred to, the ratio of the third and fourth fractions is 1.5 or less, giving grave suspicion of incompleted action when the distillation was stopped. Even if the yield of ammonia in some fraction has fallen below the limit of delicacy in nesslerising, what evidence have we that prolonged treatment would not develop a much larger amount of ammonia than that already obtained?

VII. *Applications to the Analytical Process.*

A debt of gratitude is due to Professor J. Alfred Wanklyn, as the author of a valuable method of analysis which has done much in the interest of public health. "The ammonia process," which originated in 1867, is still described in the 7th edition of "Water Analysis" (1889) essentially as in the author's first paper upon the subject. In a process of such delicacy, where the results may be influenced by a multitude of variable conditions, it is desirable that these should be accurately defined and conscientiously followed. According to the author's latest directions, 500 cc. of water are reduced to 300 cc. (to remove free ammonia) and 50 cc. of the reagent added; three measures of distillate are then collected, when "the distillation may be stopped. . . . It is necessary to nesslerise each separate 50 cc. of distillate, and to add the amounts together, in order to arrive at the total albuminoid ammonia." Besides this process, a second is described upon a scale of one-fifth, with this important modification, that the operation is "continued so long

as 10 cc. of distillate shows a sign of ammonia"; if, then, with a delicate Nessler reagent, ammonia is found in the sixth measure of distillate, the fluid must be evaporated to dryness!

But why should 350 cc. be distilled until only $\frac{3}{7}$ have gone over, while 70 cc. are distilled up to a very different limit? Probably because the *time* required to evaporate 30 cc. from the smaller retort proved insufficient for both the chemical action required and for the separation of the ammonia. Professor Wanklyn's method, as conducted in his own laboratory and by his own hands, has doubtless done valuable service, yielding good comparable results; but more definite conditions must be adopted if we would avoid discrepancies among different places and persons. Its value depends upon giving constant and comparable results under fixed conditions. For the absolute estimation of organic nitrogen, it is worthless.

It will be instructive to divide the free or albuminoid ammonia found in each measure of distillate by that found in the next, and to record the ratio so found; especially if care is taken to boil at a constant rate. According to Smart,[1] with pure animal or vegetable albuminoids, $r=2$; but if these have passed into the putrefactive condition, $r=3$; while in the case of urea (after the preliminary stage is passed) $r=1$, both for free and for albuminoid ammonia. The successful detection of recent sewage is reported, when the chemical evidence consisted in the persistent evolution of free ammonia, followed by persistent evolution of twice as much albuminoid ammonia.

The term "albuminoid ammonia," like "reverted phosphoric acid," has a technical significance determined by the method adopted in the analysis. The actual market value of reverted phosphoric acid cannot be so high under the rule for extraction at 65° as under the rule for extraction at 40°; so also 0.1 mgm. of ammonia obtained by prolonged and intense action is of less real importance than the same quantity obtained by less vigorous measures. Many modifications of the original process have been proposed; among these Breneman's[2] are worthy of special consideration. If the fluid is brought nearly to dryness, as he suggests, it may be possible to apply an exterpolation formula, such as equation (19), to the measured residue. The detailed record of

[1] Public Health (Minn.), Vol. II, No. 3, May, 1886.
[2] Jour. Amer. Chem. Soc. **8**, No. 9.

ammonia found in seven successive fractions (with greatly increased temperature and concentration at the last) may help to distinguish between different kinds of nitrogenous matter, yielding ammonia more readily and less readily; but care should be used in regard to the volume of the residue; if this is 4 cc. in one case and 7 cc. in another, there may be considerable difference in the oxidation of that comparatively inert matter which we have been led to suspect.

If the ammonia process should be applied to investigations of the relative stability of organic compounds,[1] the formulas given above may be adapted to numerous possible modifications. The use of return-flow condenser (to prolong the chemical action apart from distillation), and variations in the proportions of potash and permanganate, do not seem to have yet been tried. It is difficult to see why the alkali should always be used in so much greater excess than the oxidiser (in spite of inconvenient bumping), but it is especially strange that the distinguished author, ignoring Mallet's report of 1882, and republishing his directions without any revision, should leave the important question of *time* entirely out of account. "Suffering persecution for the sake of the truth" should make the scientist keenly alive to any truthful criticism, and ready to study the contributions of his colleagues. The "ammonia process" has now passed from one laboratory into a hundred. If "discovered about a generation before chemists were prepared for it," the time is now fully ripe to collect the testimony of those who have used it; to agree upon the general conditions of quantity, rate of boiling, and limit of distillation, and even upon such details as the matter of paper or rubber connections. When a satisfactory compromise is effected we may hope to have a uniform method of procedure and a real definition of albuminoid ammonia.

WASHINGTON, D. C., *August*, 1889.

[1] It may be of interest to compare such results with those of Dreyfus, who studied the rate of oxidation with acid solution of permanganate. Compt. rend. **105**, 523.

ON THE ACTION OF PHOSPHORUS TRICHLORIDE ON PHENOL.[1]

By Richard Anschütz and William O. Emery.

Evans and one of us[2] have recently shown that the first product of the action of antimony pentachloride on anhydrous oxalic acid very probably has the constitution

$$\begin{matrix} COOSbCl_4 \\ | \\ COOSbCl_4, \end{matrix}$$

and further, that antimony pentachloride is not decomposed by water, but rather unites with water.

The results of these investigations have disclosed to us the fundamental difference in the behavior of antimony pentachloride and phosphorus pentachloride, not only towards water, but also towards carbon compounds which contain oxygen and hydrogen.

On the other hand, phosphorus pentachloride behaves like antimony pentachloride, inasmuch as it substitutes chlorine for hydrogen in those organic compounds which contain no oxygen,[3] or oxygen in such firm combination with carbon as not to be available for the formation of phosphorus oxychloride.[4]

The compound $(COOSbCl_4)_2$ is of special interest as indicating the manner in which phosphorus pentachloride acts on substances containing the hydroxyl group. The first phase of the reaction evidently consists in the formation of compounds of analogous constitution. If the oxygen of the hydroxyl group is easy of substitution, phosphorus oxychloride is formed. If, on the other hand, the oxygen is difficult of elimination, as in the case of phenols and hydroxy acids, it might be possible to prepare substances which are constituted according to the general formulae,

$$R.O.PCl_4,\ (R.O)_2PCl_3 \text{ and } (R.O)_3PCl_3.$$

Considerations like the above have led us to attempt the preparation of the phenoxyl derivatives of phosphorus pentachloride. In the belief that these substances could be more easily prepared by an indirect method than by direct substitution of one, two or

[1] For the analytical details see the original articles in the Annalen der Chemie.

[2] Ann. Chem. (Liebig) **239**, 285.

[3] Compare for example Albert Colson and Henri Gautier, Compt. rend. **101**, 1064.

[4] Ann. Chem. (Liebig) **239**, 297.

three chlorine atoms in phosphorus pentachloride with phenoxyl rests, we have first prepared the phenoxyl derivatives of the trichloride and then treated these with chlorine.

As E. Noack[1] has shown, the following substances are formed by the action of phosphorus trichloride on phenol:

Phenyl-phosphorous dichloride, $C_6H_5OPCl_2$.
Diphenyl-phosphorous monochloride, $(C_6H_5O)_2PCl$.
Phosphorous triphenylester, $(C_6H_5O)_3P$.

The difficulties which Noack encountered in separating these substances become unimportant if the product of the reaction be rectified under greatly diminished pressure.

Phenyl-phosphorous dichloride, $C_6H_5OPCl_2$, is a colorless, highly refractive liquid, smells strongly of hydrochloric acid, and is readily decomposed by water into phenol, phosphorous and hydrochloric acids. It is easily soluble in ether, chloroform, carbon tetrachloride, and benzene, and boils under a pressure of 11 mm. at 90° (temperature of paraffin-bath 110°).

The specific gravity, determined by means of a Sprengel's pyknometer, was found to be

$$d\,\frac{20}{4} = 1.35422.$$

Diphenyl-phosphorous monochloride, $(C_6H_5O)_2PCl$, is obtained as a by-product in the preparation of the chloride $C_6H_5OPCl_2$. It is a colorless, very refractive liquid, decomposes readily in presence of moisture, and boils at 172° (temperature of paraffin-bath 190°) under a pressure of 11 mm.

The specific gravity was found to be

$$d\,\frac{20}{4} = 1.24378.$$

Phosphorous triphenylester, $(C_6H_5O)_3P$, occurs as by-product in the preparation of the two preceding chlorides; is formed exclusively by the action of three molecules of phenol on one molecule of phosphorus trichloride. The ester boils under a pressure of 11 mm. at 220°. On one occasion it was obtained as a snowy-white crystalline solid. In this condition it remained some time, but finally assumed the liquid state again.

The specific gravity we found to be

$$d\,\frac{20}{4} = 1.18428.$$

[1] Ann. Chem. (Liebig) **218**, 85.

Action of Phosphorus Pentachloride on the Phenoxyl Derivatives of Phosphorus Trichloride.

Having investigated the phenoxyl derivatives of the trichloride, we next attempted the preparation of the compounds

$$C_6H_5OPCl_4,$$
$$(C_6H_5O)_2PCl_3,$$
$$(C_6H_5O)_3PCl_2,$$

according to the equations

$$C_6H_5OPCl_2 + PCl_5 = C_6H_5OPCl_4 + PCl_3,$$
$$(C_6H_5O)_2PCl + PCl_5 = (C_6H_5O)_2PCl_3 + PCl_3,$$
$$(C_6H_5O)_3P + PCl_5 = (C_6H_5O)_3PCl_2 + PCl_3.$$

Apparently no action takes place in the cold when the substances $C_6H_5OPCl_2$, $(C_6H_5O)_2PCl$, $(C_6H_5O)_3P$ are mixed with phosphorus pentachloride. If, however, any one of them be heated with the pentachloride in molecular proportions to 100° in sealed tubes, a crystalline compound, soluble in chloroform and carbon tetrachloride, is formed.

The course of the reaction of phosphorus pentachloride on phenyl-phosphorous dichloride was very interesting. Upon heating the two substances, the pentachloride gradually disappeared; the new compound could be seen as minute oily globules, swimming about in the phosphorus trichloride, and finally the whole was found to consist of two distinct layers, one of which solidified on cooling. The liquid part boiled at 78° and was identified as phosphorus trichloride. Although the formation of phosphorus trichloride may be regarded as an indirect proof that the crystalline substance was the tetrachloride, $C_6H_5OPCl_4$, nevertheless we were unable by this method to isolate this substance in a pure condition.

We have further observed the formation of phosphorus trichloride by the action of the pentachloride on the substances $(C_6H_5O)_2PCl$ and $(C_6H_5O)_3P$, but we have not been able to separate the addition products in pure condition.

Action of Chlorine on the Phenoxyl Derivatives of Phosphorus Trichloride.

Since we were unable to prepare the phenoxyl addition-products of the trichloride by the action of phosphorus pentachloride on the substances $C_6H_5OPCl_2$, $(C_6H_5O)_2PCl$, $(C_6H_5O)_3P$, we attempted

their preparation by the action of free chlorine. The simplest reaction possible in the case of the chloride, $C_6H_5OPCl_2$, may be represented by the equation

$$C_6H_5OPCl_2 + Cl_2 = C_6H_5OPCl_4,$$

analogous to the behavior of phosphenyl chloride towards chlorine,

$$C_6H_5PCl_2 + Cl_2 = C_6H_5PCl_4;$$

and experiment has, indeed, demonstrated that the reaction does take place in the manner indicated. Owing to the extreme readiness, however, with which these addition products are decomposed by even traces of moisture, it was some time before we discovered a suitable method of purifying them.

We operated as follows: Phenyl-phosphorous dichloride, $C_6H_5OPCl_2$, was dissolved in dry ether, and a stream of dry chlorine was conducted over the surface of the solution. The chlorine was absorbed with great avidity. So much heat was generated during the operation that we considered it advisable to cool the mixture. The new compound separated as colorless crystalline leaflets. We continued to treat the ethereal solution with chlorine till the mass had assumed a faint yellow color, due to excess of chlorine. The crystals were first freed from the mother-liquor by decantation, then washed with dry ether. As the new compound is extremely hygroscopic, we were obliged to exercise the utmost care and expedition in weighing and preparing it for analysis.

Phenyl-phosphoric tetrachloride, $C_6H_5OPCl_4$, crystallises in small colorless leaves which are soluble in chloroform and carbon tetrachloride, insoluble in ether and petroleum ether. It deliquesces to an oily mass in the air. On treatment with water it decomposed violently. The aqueous solution, which contained phosphoric and hydrochloric acids, was extracted with ether and the ethereal solution rectified under diminished pressure. A comparatively small portion distilled under a pressure of 11 mm. at 245°. The distillate soon solidified to a brownish crystalline mass. Upon recrystallising from alcohol, colorless needles, fusing at 44°-45°, were obtained. Analysis showed them to have the composition $(C_6H_5O)_3PO$.

Michaelis[1] has shown that phosphenyl tetrachloride and sulphur

[1] Ann. Chem. (Liebig) **181**, 297.

dioxide yield phosphenyl oxychloride and thionyl chloride, according to the equation

$$C_6H_5PCl_4 + SO_2 = C_6H_5POCl_2 + SOCl_2.$$

We thought it of interest to ascertain the behavior of our chloride under like conditions. Upon treating the tetrachloride with sulphur dioxide and rectifying, we obtained two fractions, the first of which boiled at 78° (thionyl chloride), the second at 121°–122°, under a pressure of 11 mm. Analysis proved it to have the composition $C_6H_5OPOCl_2$. The reaction may, therefore, be expressed by the equation

$$C_6H_5OPCl_4 + SO_2 = C_6H_5OPOCl_2 + SOCl_2.$$

Diphenyl-phosphoric trichloride, $(C_6H_5O)_2PCl_3$, was prepared by treating a dry ethereal solution of the monochloride, $(C_6H_5O)_2PCl$, with chlorine. The addition product separated as a yellow oil, which gradually solidified to minute crystals. These were purified by washing with ether, and were dried in a desiccator. The trichloride is soluble in chloroform, insoluble in ether, and decomposes easily on heating. Upon treatment with water, extraction of the aqueous solution with ether and rectification in a vacuum, a fraction, boiling at 245° under a pressure of 11 mm., was obtained. This recrystallised from alcohol, fused at 44°–45°, and was found to consist of triphenyl phosphate, $(C_6H_5O)_3PO$.

We are unable to decide whether the formation of this ester in the above mentioned cases takes place in aqueous solution, or whether it is formed by heating the product of the reaction at 245° under a pressure of 11 mm.

Triphenyl-phosphoric dichloride, $(C_6H_5O)_3PCl_2$.—The formation of this compound is perfectly analogous to that of the tetrachloride, $C_6H_5OPCl_4$. We have obtained it but once as a crystalline solid. In most cases it only solidified in a freezing mixture of ether and carbonic acid. Water decomposes it into triphenyl phosphate and hydrochloric acid.

It is evident that these three addition-products,

$$C_6H_5OPCl_4,$$
$$(C_6H_5O)_2PCl_3,$$
$$(C_6H_5O)_3PCl_2,$$

are formed by the direct action of phosphorus pentachloride on phenol, analogous to the formation of the compounds

$C_6H_5OPCl_2$,
$(C_6H_5O)_2PCl$,
$(C_6H_5O)_3P$,

by the action of phosphorus trichloride on phenol. But, while these last can be easily separated and purified by rectification under diminished pressure, their chlorine addition-products are solids, which are decomposed even under diminished pressure, and further, are so hygroscopic that a separation and purification by fractional crystallisation was entirely out of the question.

Action of Bromine on the Phenoxyl Derivatives of Phosphorus Trichloride.

Although the behavior of bromine as compared with that of chlorine seemed of minor importance, we have nevertheless prepared the compounds $C_6H_5OPCl_2Br_2$ and $(C_6H_5O)_2PClBr_2$.

As is known, phosphorus trichloride yields the compound PCl_3Br_2 with great difficulty, and only in the cold. Michaelis[1] has shown that if a chlorine atom of the trichloride be replaced by the phenyl group, the tendency of phosphorus to unite with bromine is increased. It was, therefore, of interest to learn whether the phenoxyl group would produce a like effect.

Phenyl-phosphoric dichloride dibromide, $C_6H_5OPCl_2Br_2$, was prepared by treating the ethereal solution of the chloride, $C_6H_5OPCl_2$, with the dry vapor of bromine. The new compound separated as a reddish oil, which soon solidified to a yellow crystalline mass. It was purified by washing with ether. This addition product is exceedingly unstable, being readily decomposed by moisture or even when kept in sealed tubes.

Diphenyl-phosphoric monochloride dibromide, $(C_6H_5O)_2PClBr_2$. The method of preparation is perfectly analogous to that of the preceding compound, and it is equally unstable.

Action of Sulphur on the Phenoxyl Derivatives of Phosphorus Trichloride.

In our investigations we have further studied the behavior of the substances $C_6H_5OPCl_2$, $(C_6H_5O)_2PCl$, and $(C_6H_5O)_3P$ towards sulphur. Experiment has shown that phosphorus trichloride unites with sulphur only when heated in sealed tubes at 130°. We have found that a higher temperature is necessary to bring

[1] Ann. Chem. (Liebig) **181**, 298.

about the reaction if the chlorine of the trichloride be replaced by one or more phenoxyl groups.

Phenyl-thiophosphoric dichloride, $C_6H_5OPSCl_2$, was made by heating equal molecular weights of the chloride, $C_6H_5OPCl_2$, and sulphur a short time at 190°. The reaction appears to begin at about 160°; is not complete, however, below 190°. The compound is formed according to the equation

$$C_6H_5OPCl_2 + S = C_6H_5OPSCl_2.$$

The product was purified by rectifying under diminished pressure. The new compound boiled at 119°–120° (temperature of paraffin-bath 140°) under a pressure of 11 mm., and had a specific gravity, $d\,\frac{20}{4} = 1.40593$.

It is a colorless, highly refractive liquid, easily soluble in ether and chloroform.

We endeavored to prepare the compounds $C_6H_5OPSCl_2$ and $(C_6H_5O)_2PSCl$ by the action of phosphorus thiochloride on phenol, according to the equations

$$C_6H_5OH + PSCl_3 = C_6H_5OPSCl_2 + HCl,$$
$$2C_6H_5OH + PSCl_3 = (C_6H_5O)_2PSCl + 2HCl,$$

analogous to the action of phosphorus oxychloride on phenol:

$$C_6H_5OH + POCl_3 = C_6H_5OPOCl_2 + HCl,$$
$$2C_6H_5OH + POCl_3 = (C_6H_5O)_2POCl + 2HCl.$$

A mixture of phenol and phosphorus thiochloride was heated to 170° till evolution of hydrochloric acid had ceased. Upon rectifying the product, we were unable to detect even traces of the compounds $C_6H_5OPSCl_2$ and $(C_6H_5O)_2PSCl$. The neutral ester of thiophosphoric acid seemed to be the only product of this reaction.

From this we conclude that the dichloride, $C_6H_5OPSCl_2$, as well as the monochloride, $(C_6H_5O)_2PSCl$, have a greater tendency to react with phenol than phosphorus thiochloride, according to the equations

$$C_6H_5OPSCl_2 + 2C_6H_5OH = (C_6H_5O)_2PS + 2HCl,$$
$$(C_6H_5O)_2PSCl + C_6H_5OH = (C_6H_5O)_2PS + HCl.$$

Diphenyl-thiophosphoric monochloride, $(C_6H_5O)_2PSCl$, was prepared by heating molecular weights of the chloride, $(C_6H_5O)_2PCl$, and sulphur a short time at 190°. The product, purified by dis-

tillation, had a melting point of 63°–64°, and a boiling point of 194° under a pressure of 11 mm.

Triphenyl-thiophosphate, $(C_6H_5O)_3PS$, we obtained by heating molecular weights of the ester, $(C_6H_5O)_3P$, and sulphur at 190°. It crystallises in needles, which melt at 49°–50°, and boil at 245° under a pressure of 11 mm. The specific gravity was found to be

$$d\,\frac{20}{4} = 1.24411.$$

This ester was first obtained by Schwarze,[1] by the action of phosphorus sulphochloride on phenol. We have repeated his experiments and can corroborate his statements.

The striking similarity of triphenyl phosphate, $(C_6H_5O)_3PO$, to triphenyl thiophosphate, $(C_6H_5O)_3PS$, in melting and boiling points led us to compare the first products of the action of phosphorus oxychloride and phosphorus thiochloride on phenol. We prepared the compounds $C_6H_5OPOCl_2$ and $(C_6H_5O)_2POCl$ according to the directions of Jacobsen,[2] and rectified them under diminished pressure. The following table renders easy a comparison of the substances in question:

Formula.	Boiling Point.	Spec. Grav. and Melt. Pt.
$C_6H_5OPOCl_2$	116°–117° by 13–14 mm. pressure	$d\,\frac{20}{4} = 1.41214$
$C_6H_5OPSCl_2$	119–120 " 11 " "	$d\,\frac{20}{4} = 1.40593$
$(C_6H_5O)_2POCl$	195 " 13–14 " "	$d\,\frac{20}{4} = 1.29604$
$(C_6H_5O)_2PSCl$	194 " 11 " "	Melt. pt. 63°–64°
$(C_6H_5O)_3PO$	245 " " " "	" 45
$(C_6H_5O)_3PS$	245 " " " "	" 49–50

It will be readily seen from the above that the introduction of a sulphur atom in place of a corresponding oxygen atom in the chloride, $C_6H_5OPOCl_2$, causes but a slight raising of the boiling point as well as but a slight decrease in the specific gravity. Diphenyl-phosphoric monochloride and diphenyl thiophosphoric monochloride have very nearly the same boiling points under the same pressure. The former is, however, a liquid, while the latter is a solid. Triphenyl phosphate and triphenyl thiophosphate have identical boiling points under the same pressure, and the melting points lie but 4° apart.

The change in the properties, brought about by the introduction of a sulphur atom in place of a corresponding oxygen atom, appears to be the smaller, the larger the molecule of the organic compound in which the change occurs.

[1] Ann. Chem. (Liebig) **127**, 157. [2] Ber. d. chem. Ges. **8**, 1521.

Of the new compounds described in this paper, the tetrachloride, $C_6H_5OPCl_4$, seemed to possess the greatest theoretical interest. Although we have thus far been unable to prove it to be the first product of the action of phosphorus pentachloride on phenol, and were only able to prepare it by an indirect method, still we do not for a moment doubt that it is the first product in the above mentioned reaction.

If we assume the compound $C_6H_5OPCl_4$ to be the first product of the action of phosphorus pentachloride on phenol, then this reaction speaks very strongly in favor of the pentavalence of phosphorus in phosphorus pentachloride.

The existence of this compound $C_6H_5OPCl_4$ affords an entirely new view of the manner in which phosphorus pentachloride acts on all hydroxyl compounds. We may assume that the first phase of such a reaction consists in the formation of substances constituted according to the general formula,

$$R'OPCl_4.$$

If the oxygen atom be loosely bound to the radical R', the second phase of the reaction would consist in the substitution of chlorine for oxygen and the formation of phosphorus oxychloride.

ON THE ACTION OF PHOSPHORUS TRICHLORIDE ON SALICYLIC ACID.[1]

By Richard Anschütz and William O. Emery.

After the investigations of Moore and one of us[2] had to a certain extent explained the manner in which phosphorus pentachloride reacts with salicylic acid, it seemed to be of particular interest to study the behavior of phosphorus trichloride towards this acid. As has been shown, the pentachloride acts not only on the phenol- but also on the carboxyl-hydroxyl. We could not with certainty predict how the trichloride would behave towards salicylic acid, and indeed a very remarkable substance results, the formation of which will be described below. Several preliminary

[1] For the analytical details see original articles in the Annalen der Chemie.

[2] Ann. Chem. (Liebig) **228**, 308; **239**, 314. This Journal **10**, 296.

experiments had shown that salicylic acid reacts with phosphorus trichloride, and that the first product, obtained by the employment of equivalent molecular weights, can be isolated; that, however, the yield of the new compound may be essentially increased if an excess of the trichloride be employed. Phosphorus trichloride and salicylic acid do not apparently react in the cold. No hydrochloric acid is given off in any appreciable quantity before the paraffin-bath, in which the mixture is heated, has attained a temperature of 70°. We operated as follows: 50 grams of freshly distilled phosphorus trichloride and 24 grams of absolutely dry salicylic acid were brought into a distilling flask connected with an inverted condenser, and the mixture gradually heated to 70°. The escaping hydrochloric acid was conducted into a weighed flask containing water. The rate of evolution could be easily regulated by raising or lowering the temperature of the bath. After heating two hours, the reaction was practically at an end, though minute quantities of gas continued to be given off on longer heating. We have found that the largest yield of the new compound is obtained by keeping the temperature between 70° and 85°. We rectified the colorless product of the reaction first under ordinary pressure, whereby the excess of phosphorus trichloride was separated, then under greatly reduced pressure. The new product distilled under a pressure of 11 mm. at 127° (temperature of paraffin-bath 150°), and soon solidified to beautiful transparent crystals in the well cooled receiver. Analysis as well as the quantitative course of the reaction established the formula $C_7H_4O_3PCl$. The reaction can be expressed by the equation

$$C_6H_4\begin{cases}(1)\ COOH\\(2)\ OH\end{cases} + PCl_3 = C_7H_4O_3PCl + 2HCl.$$

We shall designate the new substance as *salicylo-phosphorous monochloride*, without thereby desiring to express an opinion concerning its constitution. The pure chloride melts at 36°–37°, boils at 127° under a pressure of about 11 mm., is easily soluble in ether, chloroform, and benzene, and smells, like many acid chlorides, of hydrochloric acid. It is decomposed violently by water into salicylic, phosphorous, and hydrochloric acids. An attempt to distill the substance under ordinary pressure showed that decomposition takes place at about 245°. It unites readily with chlorine and bromine, and reacts with phosphorus pentachloride, forming phosphorus trichloride and a substance of the composition $C_7H_4O_3PCl_5$.

Behavior of Salicylo-phosphorous Monochloride towards Phosphorus Pentachloride.

If the chloride be mixed with a molecular equivalent of phosphorus pentachloride, an energetic reaction takes place, the entire mass liquefies, and phosphorus trichloride, one of the resulting products, distills. The slightly yellow-colored liquid was rectified under diminished pressure. Two fractions were obtained, the first boiling at 78° and consisting of phosphorus trichloride, the second boiling at 168° (temperature of paraffin-bath 190°) under a pressure of about 11 mm. Analysis of this fraction showed that the substance has the same composition as that product obtained by the direct action of phosphorus pentachloride on salicylic acid, namely, o-$C_7H_4O_2PCl_3$. The formation may be represented by the equation

$$o\text{-}C_7H_4O_2PCl + PCl_5 = o\text{-}C_7H_4O_2PCl_3 + PCl_3.$$

It occurred to us from the behavior of the chloride $C_7H_4O_2PCl$ towards phosphorus pentachloride, that perhaps free chlorine or bromine would act in a similar manner.

Behavior of Salicylo-phosphorous Monochloride towards Chlorine and Bromine.

If dry chlorine be conducted over the chloride $C_7H_4O_2PCl$, it is absorbed with great energy and without evolution of gas. 19.0 grams chloride absorbed 6.7 grams chlorine (theory 6.6 grams). Towards the end of the operation the liquid assumed a yellowish color, due to an excess of chlorine. We can express the reaction as follows:

$$C_7H_4O_2PCl + Cl_2 = C_7H_4O_2PCl_3.$$

The product was rectified under diminished pressure. The main portion boiled constantly at 168° (temperature of paraffin-bath 190°) under a pressure of about 11 mm., and was found to be identical with those chlorides obtained by the action of phosphorus pentachloride on the chloride $C_7H_4O_2PCl$, or by the action of phosphorus pentachloride on salicylic acid.

The identity in the peculiarities of these chlorides will be seen from the following table:

	Boiling Point under about 11 mm.	Specific Gravity.
I. $C_7H_4O_2PCl_3$ from salicylic acid and PCl_5,	168° (temp. of bath 190°),	$d\,\frac{20}{4} = 1.55873$.
II. $C_7H_4O_2PCl_3$ from $C_7H_4O_2PCl$ and PCl_5,	168° (temp. of bath 190°),	$d\,\frac{20}{4} = 1.55868$.

Further, both chlorides exhibit similarity in their behavior towards water. As Moore and one of us[1] have already shown that the acid $C_7H_4O_3P(OH)_3$ could not be obtained in a pure condition from the chloride I with excess of water, we dissolved the chlorides I and II in dry benzene, and to each molecule of chloride added three molecules of water. In 24 hours the pure acid $C_7H_4O_3P(OH)_3$ had separated from the solutions. The acid from chloride I melted at 140°, while that from chloride II melted at 141°–142°. From these facts it follows that the two chlorides I and II are identical.

Not only chlorine but also bromine is absorbed with great avidity by the chloride $C_7H_4O_3PCl$. We added bromine till the resulting product had assumed a slight red color, an indication that the reaction was at an end. The formation of the new compound was accompanied by great evolution of heat; it was therefore found expedient to cool the substances during the operation. From the following data it will be seen that for every molecule of the chloride exactly one molecule of bromine was absorbed.

Experiment I. 14.2 grams chloride absorbed 10.8 grams bromine (theory 11.2).

Experiment II. 15 grams chloride absorbed 11.8 grams bromine (theory 11.9).

The reaction may evidently be expressed by the equation

$$C_7H_4O_3PCl + Br_2 = C_7H_4O_3PClBr_2.$$

The new product, purified by rectification, boiled under a pressure of about 11 mm. at 185°–188°. It is a heavy, colorless, highly refractive liquid, and was found to have the specific gravity

$$d\,\frac{20}{4} = 1.88522.$$

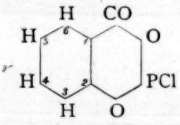
On the Constitution of Salicylo-phosphorous Monochloride and some of its Derivatives.

As regards the constitution of the compound $C_7H_4O_3PCl$, but two formulae can come under consideration if we keep in view its method of formation, change and decomposition:

I. $C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl.$ II. $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPO\end{cases}$

[1] Ann. Chem. (Liebig) **239**, 317.

According to formula I, the substance is an ortho-condensation-product. The bivalent rest PCl is joined to the carboxyl-oxygen atom as well as to the phenoxyl-oxygen atom, whereby a new ring consisting of six atoms is formed:



If the first constitutional formula be correct for the compound obtained by the action of phosphorus trichloride on salicylic acid, then by the action of phosphorus pentachloride or chlorine as well as bromine, two isomeric chlorides or bromides might be formed:

(*a*). $C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl_3$. (*b*). $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases}$.

(*a'*). $C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PClBr_2$. (*b'*). $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOBr_2\end{cases}$.

If formula II be correct, then only the formulae (*b*) and (*b'*) would come under consideration.

As far as the methods of formation of these compounds $C_7H_4O_3PCl_3$ and $C_7H_4O_3PClBr_2$, as well as their behavior towards water are concerned, both formulae (*a*) and (*b*) are possible, and it is by no means improbable that, by the action of chlorine or bromine on the chloride $C_7H_4O_3PCl$, substances constituted like (*a*) and (*a'*) are first formed, which, on heating or distilling, or perhaps in the moment of formation, are changed into the compounds (*b*) and (*b'*).

Notwithstanding our inability thus far to discover proofs that would establish the constitution of these substances beyond a doubt, we are inclined to look upon the chloride $C_7H_4O_3PCl$ as having the ring-formula

$$C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl,$$

while, on the other hand, we believe the chloride $C_7H_4O_3PCl_3$ to have the constitution

$$C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases}.$$

If the ring-formula be correct for the chloride $C_7H_4O_2PCl$, the action of phosphorus trichloride on salicylic acid is, to a certain extent, analogous to that of antimony pentachloride on oxalic acid:

$$C_6H_4\begin{cases}(1)\ COOH\\(2)\ OH\end{cases} + PCl_3 = C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl + 2HCl;$$

$$\begin{matrix}COOH\\|\\COOH\end{matrix} + 2SbCl_5 = \begin{matrix}COOSbCl_4\\|\\COOSbCl_4\end{matrix} + 2HCl.$$

However, as above stated, positive proofs that would establish the constitution of both chlorides are at present wanting. Neither by the action of methyl alcohol nor of phenol on the chloride *o*-$C_7H_4O_2PCl_3$ were we able to discover a smooth reaction.

But little better results were obtained by the action of zinc ethyl on the chloride $C_7H_4O_2PCl$. Upon treating the product of the reaction with potash solution, the unmistakable odor of the phosphines became very apparent. This fact seems to indicate that the chlorine in the chloride $C_7H_4O_2PCl$ is joined to the phosphorus atom.

The reason which leads us to prefer the formula

I. $C_6H_4\begin{cases}(1)\ COCl\\(2)\ OPOCl_2\end{cases}$ to the formula II. $C_6H_4\begin{cases}(1)\ COO\\(2)\ O\end{cases}>PCl_3$

lies in the comparison of the peculiarities of this chloride with those of the compound $(C_6H_5O)_2PCl_3$. In case the chloride *o*-$C_7H_4O_2PCl_3$ was constituted according to formula II, one might reasonably expect that it would easily decompose by distillation under diminished pressure, a behavior analogous to that of the chloride $(C_6H_5O)_2PCl_3$, which has already been described in the preceding paper. It does not, however, decompose; on the contrary, it may be distilled under greatly diminished pressure, and is at ordinary temperature liquid, while all the addition products of chlorine on

$C_6H_5OPCl_2$	$C_6H_5OPCl_4$
$(C_6H_5O)_2PCl$, that is, the compounds	$(C_6H_5O)_2PCl_5$,
$(C_6H_5O)_3P$	$(C_6H_5O)_3PCl_2$

are solids and are easily decomposed on heating under ordinary as well as diminished pressure. We are, therefore, of the opinion that the compound *o*-$C_7H_4O_2PCl_3$ is to be regarded as a derivative of phosphorus oxychloride rather than as a derivative of phosphorus pentachloride.

Chemical Laboratory, University of Bonn, *June* 1, 1889.

ON THE CONSTITUTION OF LAPACHIC ACID AND ITS DERIVATIVES.[1]

(Preliminary Communication.)

By Samuel C. Hooker and Wm. H. Greene.

In 1857, Arnoudon[2] described, under the name taiguic acid, a yellow coloring matter existing in the Taigu wood of Paraguay; nine years later, Stein[3] described as greenhartin a similar matter which he had extracted from the greenheart of Surinam. In 1879, Paterno[4] proved the identity of these substances with the lapachic acid obtained by Siewert from the Lapacho tree of South America. Finally, we have recently found the same substance in a South African wood, the Bethabarra.[5]

Paterno,[6] in an admirable research published in 1882, has assigned to lapachic acid, with a very great degree of probability, the following constitutional formula:

$$C_{10}H_4\begin{cases}O_2\\ CH=CH-C_5H_7.\\ OH\end{cases}$$

Amylene-oxy-naphthaquinone.

The results from which this formula is mainly deduced are the following:

Lapachic acid gives a series of stable salts, but all experiments failed to reveal the true acid group, COOH.

On distillation with zinc dust, naphthalene and isobutylene were obtained.

On oxidation with nitric acid, phthalic acid was formed.

By reducing agents, a hydrolapachic acid was obtained, which rapidly absorbed oxygen, becoming reconverted into lapachic acid.

A monacetyl derivative was obtained.

Hydriodic acid and phosphorus gave a liquid hydrocarbon, which was taken to be amyl-naphthalene.

In the course of the study of this acid, Paterno prepared several compounds, which he was able to explain satisfactorily only by the assumption that two molecules of the acid had taken part in the formation of each of their molecules.

[1] Read at the meeting of the Chemical Section of the Franklin Institute, held Tuesday, May 21, 1889. [2] Comptes rendus **41**, 1152. [3] J. prak. Chemie **99**. [4] Gaz. Chim. Ital. **9**, 506. [5] This Journal **11**, 267. [6] Gaz. Chim. Ital. **12**, 337-392.

By the action of concentrated sulphuric acid on lapachic acid, a compound crystallising in beautiful red needles is formed, which has precisely the same percentage composition as lapachic acid. This compound, which is known as lapachone, was assigned the following formula by Paterno,

$$OH.C_{10}H_4(C_5H_9)\begin{matrix}O.O\\O.O\end{matrix}C_{10}H_4(C_5H_9).OH.$$

Lapachone is insoluble in alkaline carbonates; it is soluble in caustic alkalies only after boiling for some time. According to Paterno, it separates from the alkaline solution on cooling, and is almost completely precipitated unchanged on the addition of acids.

While recently engaged on the study of the coloring matter of Bethabarra wood, subsequently proved by us to be lapachic acid, we obtained an orange-red quinone-like substance. In the course of our experiments with this compound we observed a number of reactions which, when we had afterwards identified the compound as lapachone, did not agree with Paterno's view of its constitution.

We found that lapachone shows many of the characteristics of a quinone. It gives a white crystalline compound with acid sodic sulphite, which is reconverted by acids and alkalies into the original substance. It forms compounds with hydroxylamine and ammonia with great readiness, and gives the quinone color reaction of Bamberger.

These reactions are obviously not reconcilable with the formula given above, and point to the probability that lapachone is $C_{15}H_{14}O_3$ and not $C_{30}H_{28}O_6$.

A determination of the molecular weight of lapachone, by Raoult's method, gave figures confirming this supposition, thus proving that only one molecule of lapachic acid is concerned in its formation, a result borne out by other facts.

Calculated for Paterno's formula $C_{30}H_{28}O_6$.	Calculated for $C_{15}H_{14}O_3$.	Found.
484	242	255

It remains, therefore, to explain how a substance having such strong acid tendencies as lapachic acid, dissolving with ease in alkaline carbonates, can be converted into an indifferent compound like lapachone, and yet retain the same percentage composition.

Although Paterno's formula of lapachic acid cannot be considered in any way proved, it lends itself well to the explanation of

the formation of lapachone, and in this way considerable indirect proof is furnished of the probable correctness of Paterno's views in regard to lapachic acid.

It seems lawful to assume that under the influence of strong mineral acids (concentrated nitric acid in the cold acts similarly to concentrated sulphuric acid, as shown by Paterno), lapachic acid takes up a molecule of water, giving rise to an intermediate compound, which is at once decomposed by the acid, again splitting off water, but in a different direction. This is shown in the following equation:

$$C_{10}H_4\begin{cases} O_2 \\ CH=CH.C_5H_7 \\ OH \end{cases} + H_2O$$

Lapachic acid.

$$= C_{10}H_4\begin{cases} O_2 \\ CH_2-CH(OH).C_5H_7 \\ OH \end{cases}$$

Oxy-hydro-lapachic acid.

$$= C_{10}H_4\begin{cases} O_2 \\ CH_2 \\ O \end{cases}\!\!>CH.C_5H_7 + H_2O.$$

Lapachone.

The fact that phthalic acid is produced by the oxidation of lapachic acid would appear to furnish proof that all the side groups are situated in the same benzene nucleus, and consequently whether lapachic acid be a derivative of α- or of β-naphthaquinone, the (OH) group must be in the ortho position to the amylene chain: this favors the probability of the occurrence of the above condensation.[1]

This view of the constitution of lapachone, *i. e.* regarding it as a derivative of naphthofurfuran, agrees very thoroughly with all its properties and reactions so far observed. It has, moreover, received direct confirmation from the result of an experiment, which was made to obtain, if possible, corroboration of our views.

Paterno states, as already mentioned, that lapachone is insoluble in caustic alkalies in the cold, but dissolves on heating, and is, in part, deposited from the filtered solution unchanged as it cools.

This observation seemed at variance with our idea of the constitution of lapachone, and we consequently carefully repeated Paterno's experiment. The insolubility of lapachone in alkaline

[1] It is, of course, possible, though scarcely probable, that lapachic acid is derived from β-β-naphthaquinone, in which case the relative positions of the amylene chain and the hydroxyl group would be the para.

carbonates and caustic alkalies in the cold is readily explained by the constitution we have assigned to it, and its solubility on boiling is best accounted for by the supposition that the furfuran ring is split by the action of potash, that one molecule of water is taken up with the formation of a salt of the compound

$$C_{10}H_4\begin{cases} O_2 \\ CH_2.CH(OH).C_3H_7 \\ OH \end{cases}$$

Oxy-hydro-lapachic acid.

which we had previously supposed to exist as an intermediate product in the formation of lapachone. This explanation proved quite satisfactory, for on neutralising with acetic acid, a red oil was obtained which, in the course of an hour or so, solidified to a yellow crystalline mass. Analysis proved it to have the expected composition. The tendency of the new substance to pass into lapachone under the influence of dilute mineral acids is very great, and hence if dilute hydrochloric acid be used for the precipitation, either a mixture of lapachone and the new compound, or lapachone only, is obtained.

We have not yet succeeded in preparing the potassium salt of the new substance in a crystalline form, but as its barium salt, which crystallises very readily in bright orange needles, closely resembles lapachone, it is not improbable that the potassium salt may have a similar appearance, which would account for Paterno's supposition that the crystals deposited on cooling and before the addition of hydrochloric acid were crystals of lapachone. It is right to add that the fusing point of these crystals was found by Paterno to be almost identical with that of lapachone.

The salts of the new compound, as might be expected, dissolve to the same intense red color as those of lapachic acid. Oxyhydrolapachic acid melts at 125°, and is very readily soluble in most ordinary solvents. It may be obtained in comparatively large crystals by spontaneous evaporation of its solution in alcohol or acetic acid.

By the action of bromine on lapachic acid in acetic acid solution, Paterno obtained a compound which he regarded as monobromlapachic acid, and to which he assigned the formula

$$C_{10}H_4\begin{cases} O_2 \\ CH=CH.C_3H_7. \\ OBr \end{cases}$$

Considering the properties of this compound and the probable constitution of lapachic acid, its formation would seem to be better explained by the supposition that an addition product is first formed, and that this, by splitting off hydrobromic acid, gives rise to the formation not of brom-lapachic acid but of brom-lapachone, thus:

$$C_{10}H_4\begin{cases}O_2\\ CH=CH.C_3H_7\\ OH\end{cases}+Br_2$$

$$=C_{10}H_4\begin{cases}O_2\\ CHBr-CHBr(C_3H_7)\\ OH\end{cases}$$

$$=C_{10}H_4\begin{cases}O_2\\ CHBr\\ O\end{cases}>CH.C_3H_7+HBr.$$

We are at present endeavoring to prove the truth of this supposition, and have already observed some important facts tending to show the correctness of our views.

The formation of several of the other compounds obtained by Paterno would appear to be better explained in a similar manner to the foregoing than by the formulae he has assigned to them. We prefer, however, to leave the discussion of these until our work has progressed further. In the meantime, we wish to say that, although we are hopeful further experiments will justify our present conclusions, we do not regard them as of necessity final, and have only been induced to make this preliminary communication to ensure to ourselves the undisturbed continuation of the work, which, owing to many causes, cannot, unfortunately, proceed with as great rapidity as we could desire.

POSTSCRIPT.—We have to-day (June 17) received from Prof. Paterno an advanced proof from No. 6 of the Gazzetta Chimica Italiana for this year, having reference to our intention, as stated in the AMERICAN CHEMICAL JOURNAL **II**, 267, of studying the constitution of lapachone. He requests that we desist from carrying out our purpose, as he is still investigating lapachic acid and its derivatives, a fact which should have been known to us, but unfortunately was not, owing to the miscarriage of a number of the Gazzetta for the current year, the only copy sent, to our knowledge, to Philadelphia. We gladly accede to Prof. Paterno's request, in full

confidence that our work has not been without service in establishing the constitution of the derivatives of lapachic acid. At the time of writing, the above paper, which was read nearly a month ago, has been already printed for private distribution among the members of the chemical section of the Franklin Institute.

REDETERMINATION OF THE ATOMIC WEIGHT OF PALLADIUM.

By E. H. Keiser.

Among all the atomic weights there are few that have been so imperfectly determined as that of palladium. In 1826 Berzelius[1] found that 100 parts of the metal united with 28.15 parts of sulphur, from which proportion the value for the atomic weight of palladium would be 113.63. This number is undoubtedly too high, and two years afterwards the same investigator[2] obtained a much lower value as the result of two analyses of potassium palladious chloride, $PdCl_2.2KCl$. Weighed quantities of the salt were heated in a stream of hydrogen, and after reduction the quantities of metallic palladium and potassium chloride remaining were determined. The following are the results of the analyses:

I. 1.757 gram $PdCl_2.2KCl$ gave .575 gram Pd and .809 gram KCl.

II. 2.606 grams $PdCl_2.2KCl$ gave .851 gram Pd and .809 gram KCl.

	I.	II.
Pd, ...	32.726	32.655
KCl, ...	46.044	45.741
Cl (by difference), .	21.230	21.604
	100.000	100.000

Calculating the atomic weight from the ratio of palladium to potassium chloride, the first analysis gives Pd = 105.7, the second Pd = 106.2.

In 1847 Quintus Icilius[3] determined the loss in weight which

[1] Poggend. Annal. **8**, 177 (1826). [2] Ibid. **13**, 454 (1828).
[3] F. W. Clarke, Recalculation of the Atomic Weights, p. 257.

potassium palladious chloride undergoes when heated in a current of hydrogen, and found as the mean of three determinations that the amount of residue was 64.81 per cent., from which the calculated value for the atomic weight of palladium is 111.88. This value is undoubtedly too high.

No other determinations of this atomic weight have been made. The values that have been adopted by those who have recalculated the atomic weights are as follows:

Meyer and Seubert, . .	(O = 15.96)	106.2
F. W. Clarke, . . .	(O = 15.96)	105.7
W. Ostwald, . . .	(O = 16)	105.9
Van der Plaats, . .	(O = 16)	106.5

As these values are calculated from the two analyses of Berzelius mentioned above, and as these analyses do not agree very closely with one another, it seemed to me to be desirable to undertake a new series of determinations of this atomic weight. It also appeared advisable to analyse a different compound from that employed by Berzelius, for the reason that, as stated in his paper, it is extremely difficult to get the potassium palladious chloride free from water. The crystallised salt when dried in a desiccator for a long time still retains water of decrepitation (verkinsterungswasser), nor can it be completely removed by drying in an air-bath at a low temperature; while if the temperature be raised, partial decomposition takes place and hydrochloric acid and palladium oxide are formed.

For the purpose of avoiding this source of error, experiments were at first made with the double chlorides of palladium and ammonium. Ammonium palladious chloride, $PdCl_2.2NH_4Cl$, and ammonium palladic chloride, $PdCl_4.2NH_4Cl$, were prepared and purified by repeated recrystallisation, and were then dried in a partial vacuum over sulphuric acid. Portions of the salts were weighed off in platinum boats and heated in an air-bath. It was found that the salts gradually lost in weight as the temperature increased, and it was impossible to obtain a constant weight at temperatures below the point of decomposition. The dried salts also proved to be very hygroscopic, they absorbed moisture so rapidly on the scale pan that it was impossible to weigh them with the accuracy that is necessary in atomic weight determinations. All hope of using these compounds was abandoned, and the same

objections were found to apply to the double chlorides of palladium and sodium. Indeed, it appears that the double chlorides of the alkali and platinum metals all contain water of decrepitation which it is extremely difficult if not impossible to remove, and which makes them unsuited for atomic weight determinations. Stas[1] gave up his attempt to determine the atomic weight of platinum by reduction of potassium platinic chloride when he found that the carefully dried salt still retained a trace of moisture. Berzelius had previously observed the same fact, and he found that the double chlorides of the alkali and other platinum metals also contain water. In some of his analyses he endeavored to remove this trace of water by heating the salts in a stream of chlorine, and this method of drying was afterwards employed by Seubert[2] in his determination of the atomic weight of iridium.

After examining the properties of a number of palladium compounds, I found that the yellow crystalline palladium diammonium chloride, which is formed whenever hydrochloric acid is added to a solution of palladium chloride in an excess of ammonia, is a much more suitable compound for the purpose of atomic weight determinations than any of those mentioned above. It possesses the advantages of being a stable compound which can be prepared in a state of great purity. It contains no water of crystallisation, nor does it retain water mechanically which cannot be removed by drying the compound in a desiccator. The salt can be dried in an air-bath without undergoing decomposition, and further, the dried compound is not hygroscopic and can be accurately weighed in the atmosphere of the balance-case. Heated in a stream of hydrogen, it at first absorbs the gas, the bright yellow color changes to black, and metallic palladium and ammonium chloride are formed. On raising the temperature, the ammonium chloride is volatilised and spongy palladium remains behind.

Preparation of Palladium Diammonium Chloride.

Metallic palladium in the form of foil was dissolved in aqua regia and the solution evaporated to dryness. The residue of palladious chloride was dissolved in dilute hydrochloric acid, and the solution, after filtering, was treated with ammonia and heated until the flesh-colored precipitate which was at first formed had been dissolved by the excess of ammonia. The liquid was then again

[1] Stas, Chemische Proportionen, 1867, p. 265. [2] Ber. d. chem. Ges. **11**, 1770.

filtered to remove a trace of ferric hydroxide, and into the filtrate hydrochloric acid gas was passed until the palladium diammonium chloride was completely precipitated. The yellow precipitate was thereupon redissolved in ammonia to separate it from any of the analogous rhodium compound which might have been present, and to the filtrate hydrochloric acid was added to reprecipitate the palladium diammonium chloride. The precipitate was dried and afterwards heated in a current of pure hydrogen. Pure spongy palladium was thus obtained, which was converted into the yellow crystalline palladium diammonium chloride by the process just described. The compound was dried at first over sulphuric acid, afterwards in the air-bath at a temperature of from 120° to 130°.

Analyses of the palladium diammonium chloride were made by weighing off portions of the dried salt in platinum boats and introducing the boats into a short combustion tube which was connected with an apparatus for the preparation of pure hydrogen. The gas was prepared by the interaction of pure zinc and dilute sulphuric acid. It was purified by passing through acid and alkaline potassium permanganate, then through concentrated sulphuric acid, over iron wire heated to a red heat, and finally over phosphorus pentoxide. After the air had been expelled from the combustion tube by the stream of hydrogen, that part of the tube which contained the platinum boat was heated gently. At a comparatively low temperature the yellow palladium diammonium chloride begins to turn black, the change is accompanied by a rapid absorption of hydrogen, and metallic palladium and ammonium chloride are formed,

$$PdN_2H_6Cl_2 + 2H = Pd + 2NH_4Cl.$$

So readily does this change take place that it is only necessary to heat one end of the boat until the action begins, because the heat of the reaction is sufficient to convert the entire quantity of the compound into metallic palladium and ammonium chloride.

After the reduction the temperature of the combustion tube was gradually raised until the ammonium chloride was all volatilised and nothing but spongy palladium remained in the boat. The finely divided palladium usually adheres together and forms a porous bar having the shape of the interior of the boat. The boat was now allowed to cool down, at first in the stream of hydrogen until it was below a red heat, then after a time the hydrogen was displaced by a current of dry air. By this means it was possible

to avoid the retention of the hydrogen by the palladium, and as the hydrogen was not displaced by the air until the temperature had fallen considerably below a red heat, it was not possible that palladium oxide should have been formed. After the boat had acquired the temperature of the air, it was removed from the combustion tube and the weight of metallic palladium remaining in it determined.

A short beam analytical balance, sensitive to $\frac{1}{10}$ milligram, and an adjusted set of weights were employed for all the weighings. The correction of the weights for buoyancy of the air was found to be smaller than the experimental errors, and was therefore omitted. From the results of the analyses the atomic weight of palladium was calculated by means of the proportion:

$$A : B :: x + 104.76 : x \quad \text{or}$$

$$x = \frac{104.76\ B}{A - B}, \text{ in which}$$

A = weight of $PdN_3H_6Cl_3$ taken,

B = " Pd found, and

$$104.76 = N_3 + H_6 + Cl_3 = (14.01 \times 2) + (1 \times 6) + (35.37 \times 2).$$

The results of the analyses are as follows:

I SERIES.

Number.	Weight of $PdN_3H_6Cl_3$ taken.	Weight of Pd obtained.	Atomic Weight.
1	.83260	.41965	106.459
2	1.72635	.86992	106.410
3	1.40280	.70670	106.355
4	1.57940	.79562	106.342
5	1.89895	.95650	106.321
6	1.48065	.74570	106.292
7	1.56015	.78585	106.322
8	1.82658	.92003	106.317
9	2.40125	1.20970	106.355
10	1.10400	.55629	106.400
11	.93310	.47010	106.366
Total,	16.74583	8.43606	[106.3520]

Mean value, 106.352 Maximum 106.459

Minimum 106.292

Difference, .167

II Series.

The palladium diammonium chloride used in this set of determinations was prepared from the metallic palladium which was obtained in the first series of determinations.

Number.	Weight of $PdN_2H_6Cl_2$ taken.	Weight of Pd obtained.	Atomic Weight.
1	2.61841	1.31900	106.340
2	2.23420	1.12561	106.366
3	1.73553	.87445	106.325
4	1.69160	.85210	106.390
5	1.72403	.86825	106.332
6	1.12222	.56535	106.286
7	1.17457	.59200	106.355
8	2.42760	1.22280	106.455
Total, .	14.72816	7.41956	[106.3503]

Mean value, 106.35

Maximum 106.455
Minimum 106.286

Difference, .169

The mean value of both series of determinations is 106.35, a number which agrees fairly well with that calculated from the second analysis of Berzelius, mentioned at the beginning of this article.

Bryn Mawr, Pa., *June*, 1889.

ON THE ACTION OF DILUTE ACIDS ON BENZOIC SULPHINIDE AND THE ANALYSIS OF COMMERCIAL SACCHARIN.

By Ira Remsen and W. M. Burton.

In the course of experiments undertaken by us for the purpose of studying the effect of nascent hydrogen on benzoic sulphinide,[1]

[1] It was hoped that a basic substance might be formed, as when phthalimide is reduced. No evidence of reduction was obtained by boiling with tin and hydrochloric acid. On the other hand, sodium amalgam causes deep-seated changes, as was shown by the abundant evolution of sulphur dioxide and hydrogen sulphide when the solution is acidified. No definite product, however, was isolated.

we noticed that when this compound is boiled with dilute hydrochloric acid and tin its sweet taste is soon destroyed. Further study showed that the change is due to the action of the acid alone, and that no reduction takes place. Two grams of the pure sulphinide were boiled with about 100 cc. hydrochloric acid diluted with fifteen times its volume of water. After forty-five minutes the sweet taste of the solution had disappeared. Pure silver oxide was then added in excess to remove the hydrochloric acid, and, after filtering, hydrogen sulphide was passed through the filtrate, when a considerable precipitate of silver sulphide was formed. On evaporating the filtrate from this, a small quantity of white crystals was deposited. These proved to be ortho-sulphamine-benzoic acid. The mother liquor was further concentrated until fine large crystals of acid ammonium ortho-sulphobenzoate were deposited. These were easily recognised by their crystalline form, melting point, and the fact that they gave off ammonia when treated with caustic alkalies. From the 2 grams of sulphinide taken we obtained about .1 gram *o*-sulphamine-benzoic acid and 1½ grams of the acid ammonium salt. It appears, therefore, that when benzoic sulphinide is boiled with hydrochloric acid it is converted into *o*-sulphamine-benzoic acid and acid ammonium *o*-sulphobenzoate. Further experiments showed that by continued boiling with hydrochloric acid all the *o*-sulphamine acid is converted into the acid ammonium salt. Probably the first result of the action of the hydrochloric acid is represented by this equation:

$$C_6H_4\begin{cases}CO\\SO_2\end{cases}NH + H_2O = C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}.$$

Then by continued boiling the second change takes place as represented in this equation:

$$C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases} + H_2O = C_6H_4\begin{cases}COOH\\SO_2ONH_4\end{cases}.$$

A series of experiments was now undertaken to determine what strength of acid and what conditions are best for the rapid and complete conversion of the sulphinide into the acid ammonium salt. Hydrochloric acid of various degrees of concentration was prepared by diluting the pure strong acid (sp. gr. 1.17) with different amounts of water. In each experiment 100 cc. of a dilute acid of known strength were placed in a balloon flask of 250 cc. capacity, and the flask connected with an upright condenser. The

mixture was gently boiled, and from time to time it was tested by the taste to ascertain just when the sweet taste disappeared. The test is as refined as any that could be devised, as the presence of a weighable quantity of the sulphinide in the solution can be detected in this way without difficulty. Of course, the disappearance of the sweet taste is not proof that the sulphinide has been converted into the acid ammonium salt, for, as we have seen, some *o*-sulphaminebenzoic acid is always formed. Still the quantity of this formed is quite insignificant.

The following table gives the results of the experiments:

Concentration of Acid.			Time.
HCl		H_2O	
1	:	100	6 hours,
1	:	75	3 " 15 min.
1	:	50	2 " 15 "
1	:	25	2 "
1	:	20	1 "
1	:	15	45 min.
1	:	10	30 "
1	:	5	40 "
1	:	8	30 "

According to this, the hydration of benzoic sulphinide is best effected by hydrochloric acid prepared by diluting the pure strong acid of specific gravity 1.17 with 8–10 parts water. Special experiments showed that the change is effected slowly by the concentrated acid on a water-bath, though by heating in a closed vessel to 150° the change takes place rapidly.

Analysis of Commercial Saccharin.

The easy conversion of benzoic sulphinide into a substance which is readily soluble in water suggested a method for determining the amount of the sulphinide contained in commercial saccharin. As is well known, this product is manufactured by oxidising toluene sulphonamide. According to the statements made in regard to the process, the orthotoluene sulphonchloride is separated from the para-compound and is then converted into the amide, which is oxidised with potassium permanganate. It is, however, a difficult and expensive matter to effect a complete separation of the two chlorides. If the separation is not complete, then both sulphonamides will of course be formed, and the separation of these is even more difficult than that of the chlorides. When the mixture of the two amides is oxidised with potassium

permanganate, the ortho-amide is converted mainly into the sulphinide, and, to some extent, varying with the conditions, into acid potassium ortho-sulphobenzoate, while the para-amide is converted into para-sulphamine-benzoic acid. A consideration of these facts makes it appear probable that commercial saccharin contains at least the three substances, benzoic sulphinide, para-sulphamine benzoic acid, and acid potassium ortho-sulphobenzoate, with perhaps some of the sulphonamides remaining unoxidised. Attempts made in this laboratory to prepare pure benzoic sulphinide from commercial saccharin have repeatedly shown that the amount of para-sulphamine acid present in it is very considerable, amounting as nearly as could be judged to about 50 per cent. of the whole. But no careful experiments were undertaken to determine the amount, owing to the lack of a suitable method of analysis. Briefly stated, the method which we used consists in boiling the commercial saccharin with an excess of hydrochloric acid prepared by diluting the pure strong acid with eight times its volume of water. By this means the sulphinide is converted quantitatively into the acid ammonium salt of *o*-sulphobenzoic acid, while the *p*-sulphamine-benzoic acid and the acid potassium salt of *o*-sulphobenzoic acid which are always present in commercial saccharin remain unchanged. The para-acid is very difficultly soluble in cold water, while the potassium and ammonium salts of *o*-sulphobenzoic acid are very easily soluble in cold water. If, therefore, the liquid obtained by boiling commercial saccharin with hydrochloric acid is evaporated to a small volume and allowed to cool, practically all the para-sulphamine-benzoic acid will be on the filter while the potassium and ammonium salts of *o*-sulphobenzoic acid will be in the filtrate. This can then be evaporated to dryness and the weight of the salts determined. By determining the potassium in the residue, and calculating the weight of acid potassium salt, the weight of the acid ammonium salt can be estimated, and from this the weight of the benzoic sulphinide corresponding to it. It may be questioned whether it is fair to assume that all the potassium found is present in the form of the acid potassium salt of *o*-sulphobenzoic acid. With reference to this point we can only say that we excluded the salts of mineral acids; that in working over large quantities, amounting to several kilograms of the commercial saccharin, we have isolated the acid potassium salt in well-formed crystals, and that we have never found any other potassium salt. That there was no ortho-com-

pound left on the filter was shown by special experiments. The para-acid was compared with pure acid obtained by oxidising *p*-toluene sulphonamide. The two were found to conduct themselves alike as regards fusion, solubility, and crystallisation. It was fused with potassium hydroxide and converted into para-oxybenzoic acid, melting sharply and crystallising well in the characteristic form. Not a trace of salicylic acid was formed, ferric chloride producing no marked change in color.

The para-acid is not changed by boiling with dilute hydrochloric acid.

The most convenient method for the analysis of commercial saccharin was found to be as follows:

About 2 grams saccharin is placed in a balloon flask of 250 cc. capacity, 100 cc. hydrochloric acid (1–8) added, and the flask connected with an inverted condenser. The mixture is then gently boiled for an hour. The clear solution in the flask is then transferred to an evaporating dish and evaporated to about 15 cc. This is allowed to stand for several hours, when the parasulphamine acid separates in glistening scales. This is collected on a filter previously dried to a constant weight at 80°. The acid is thoroughly washed with cold water, and then dried to constant weight at 80°. The filtrate and washings are collected in a weighed glass evaporating dish, evaporated to dryness and weighed. The amount of potassium in this residue is determined by treating a weighed portion of it in a platinum crucible with strong sulphuric acid, and weighing as potassium sulphate. Five parallel analyses of two samples of saccharin were made, and the results are given in the tables below. Sample I was imported in 1887 and sample II in 1888.

Analysis of Sample I.

No.	Amt. Taken.	*p*-Acid.	Ac.K Salt.	Ac.NH_4 Salt	= Sulphinide.
1.	1.3605	0.6693	0.0979	0.6906	0.5771
2.	1.9304	0.9721	0.1340	0.9867	0.8245
3.	2.3258	1.1326	0.1677	1.2021	1.0044
4.	1.7608	0.8980	0.1254	0.9229	0.7711
5.	2.1354	1.0837	0.1520	1.0780	0.9007

Analysis of Sample II.

No.	Amt. Taken.	*p*-Acid.	Ac.K Salt.	Ac.NH_4 Salt	= Sulphinide.
1.	2.2684	0.9933	0.1837	1.3209	1.1037
2.	2.2860	1.0058	0.1778	1.2864	1.0765
3.	2.1358	0.9666	0.1687	1.2256	1.0241
4.	1.8756	0.8155	0.1499	1.0823	0.9044
5.	2.0955	0.9383	0.1674	1.2170	1.0169

The above results when expressed in percentages give the following figures:

Composition of Sample I.

	I.	II.	III.	IV.	V.
Parasulphamine-benzoic acid,	49.20	50.36	48.70	51.01	50.75
Benzoic sulphinide,	42.42	42.71	43.19	43.80	42.18
Ac. potass. *o*-sulphobenzoate,	7.20	6.94	7.21	7.12	7.12

Composition of Sample II.

	I.	II.	III.	IV.	V.
Parasulphamine-benzoic acid,	43.79	45.13	45.26	43.48	44.78
Benzoic sulphinide,	48.65	48.29	47.95	48.22	48.53
Ac. potass. *o*-sulphobenzoate,	8.10	7.98	7.90	7.99	7.99

In analyses of IV and V of each sample the potassium was not determined, but the mean of the results obtained in analyses I, II and III was taken. While owing to the nature of the substances and the imperfection of the method the results are not as concordant as could be desired, they are nevertheless close enough to give confidence in the method, and it may be asserted with perfect confidence that the figures are very near the truth.

It follows that the substance known commercially as *saccharin is a mixture of para-sulphamine-benzoic acid, benzoic sulphinide, and acid potassium o-sulphobenzoate, and that the amount of the sulphinide present is somewhat less than* 50 *per cent.*

As is well known, the only one of the three constituents of saccharin which is regarded as having any commercial value is the sulphinide, and its value is due to the fact that it has about three hundred times the sweetening power of cane sugar. We think that this estimate is somewhat too high, but assuming it to be correct, and assuming further that only about 50 per cent. of the commercial substance is sulphinide, an assumption that is fully justified by our analyses, it follows that commercial saccharin instead of being "three hundred times as sweet as sugar" is not more, and is probably considerably less, than one hundred and fifty times "as sweet as sugar." It would, we think, be nearer the truth to say that commercial saccharin has a sweetening power about one hundred and twenty-five times as great as that of cane sugar.

ON THE DETERMINATION OF CHLORINE IN WATER.

By Allen Hazen.

Chlorine is almost always determined in water by titration with silver nitrate solution, using potassium chromate as indicator. It has been my practice to titrate fifty cubic centimeters of water or sewage in a porcelain dish with a silver solution of such strength that one cubic centimeter corresponds to half a milligram of chlorine, so that each cubic centimeter used represents one part of chlorine in 100,000. The results commonly obtained by this method are somewhat too high, owing to the fact that the red color of silver chromate does not become perceptible until a certain excess of silver has been added, and this excess, as will be shown, is much too large to be neglected when close work is desired.

I have made a large number of experiments to ascertain the amount of excess of silver solution required to give an end-point under various conditions of titration, and especially to find the influence of the volume of the liquid titrated, the amount of chromate used, and the amount of precipitated silver chloride present. I have found that under constant conditions the required excess is constant, and that by making the proper corrections very accurate results can be obtained, even in widely differing conditions of titration.

The general method by which these experiments have been carried out is as follows: Silver and chlorine solutions were made by dissolving the theoretical quantities of pure silver nitrate and sodium chloride in distilled water. A solution of potassium chromate, free from chlorine, was used which contained 0.12 gram per cubic centimeter. Measured quantities of chlorine and chromate solutions were put into a white porcelain dish with distilled water, and titrated with the silver solution. The amount of silver solution required was in every case more than an equivalent of the salt used. The excess is the amount of silver solution required to produce an end-point under the conditions of the experiment. In all cases I have not gone beyond an end-point which was as faint as could be seen with certainty after some seconds, there being always a second dish of chromate, for com-

parison, by the side of that in which the titration is made. The solution should not be so concentrated as to make the precipitated silver chloride coagulate, as in that case the required excess is somewhat greater than otherwise.

The amount of chromate used has a considerable influence on the result, especially in a large volume. In general, it may be said that the greater the amount of chromate used, the smaller will be the required excess of silver; but when the quantity has reached a certain point, the advantage gained by any further increase is more than overcome by the increase in color, which obscures the exact end-point. I have found 0.0010 gram potassium chromate per cubic centimeter of liquid titrated (a much larger amount than is generally recommended) to be a suitable quantity. This is enough to give most of the advantage due to increased quantity, while the end-point remains very sharp. In practice I use 0.06 gram of potassium chromate in all cases, even when the volume of liquid titrated is small; the end-point is quite as sharp as with a smaller quantity.

The following titrations show the excess of silver solution required when different quantities of chromate are used, all other conditions being the same:

NaCl sol. taken.	K_2CrO_4 grams.	Vol. of liquid titrated.	$AgNO_3$ sol. required.	Excess.
2 cc.	.004	50 cc.	2.45	.45
"	.008	"	2.35	.35
"	.016	"	2.27	.27
"	.030	"	2.20	.20
"	.060	"	2.16	.16
"	.120	"	2.15	.15

The volume of the liquid titrated has also an influence on the result. (The volume may be easily determined, after titration, by pouring the liquid into a graduate.) The required excess of silver solution increases regularly with the volume, and when 0.06 gram chromate is used, and the volume is not more than 60 cc., this excess may be represented by the formula $x = .003\ v + .02$, where v is the volume of liquid at the end of the titration in cubic centimeters. Thus with a volume of 3 cc. the correction is .03 cc., while with a volume of 50 cc. the correction is .17 cc.

The following titrations were made in different volumes, all other conditions being the same:

NaCl sol. taken.	K_2CrO_4 used.	Vol. of liquid.	$AgNO_3$ sol. required.	Excess.
2 cc.	.06 gr.	4 cc.	2.03 cc.	.03 cc.
"	"	10	2.05	.05
"	"	20	2.07	.07
"	"	30	2.10	.10
"	"	40	2.14	.14
"	"	50	2.17	.17
"	"	100	2.35	.35

The amount of precipitated silver chloride present influences the result. The required excess of silver solution, in addition to the correction for volume, increases regularly with the amount of precipitated silver chloride, and is nearly proportional to the amount of silver solution used. The correction is nearly one per cent. of the volume of the silver solution. The most convenient way to apply this correction is to use a silver solution containing one per cent. more than the theoretical amount of silver. If the silver solution is standardised against sodium chloride, it will be of this strength, and no correction will be required for the amount of precipitate. If the amount of chlorine titrated is very low the results are somewhat irregular, so that if less than 1 cc. of silver solution is required for 50 cc. of water, I prefer to run in 1 cc. of salt solution and deduct the equivalent of silver solution from the result. The influence of the amount of precipitated silver chloride is shown by the following titrations:

NaCl sol. taken.	K_2CrO_4 used.	Vol. of liquid.	$AgNO_3$ sol. required.	Excess.
0.0 cc.	.06 gr.	50 cc.	.10 cc.	.10 cc.
.2	"	"	.30	.10
.6	"	"	.72	.12
1.0	"	"	1.16	.16
2.99	"	"	3.17	.18
5.98	"	"	6.19	.21
9.97	"	"	10.22	.25

The silver solution used for these titrations was very carefully made to contain exactly the theoretical quantity of silver. A portion of this solution was precipitated with its equivalent of salt solution; to the clear liquid, separated from the precipitate, was added a small amount of salt solution and chromate, and titrated with silver solution. The amount required was the same as when distilled water was used, all other conditions being the same.

Although the original silver solution was made by dissolving the theoretical quantity of pure silver nitrate in water, it is practically more convenient and better to depend upon titrations of salt

solution for its strength, always making the correction for volume. As has been shown, a solution made in this way will require no correction for precipitated silver chloride, but the correction for volume must invariably be applied. As this correction is not at all proportional to the amount of silver solution used, accurate results cannot be obtained by using a stronger solution and omitting this correction.

A few titrations of salt solution in varying amounts of water, taken at random from my note-book, are as follows. The silver solution used was standardised against salt solution, and the correction for volume made. In each case .06 gram chromate was used.

Milligrams Cl taken.	Vol. of liquid.	$AgNO_3$ sol. required.	Corrected for volume.	Milligrams Cl found.
5	16 cc.	10.06	9.99	4.995
5	50	10.18	10.01	5.005
1	40	2.12	1.98	.99
1	70	2.20	1.99	.995
.94	80	2.10	1.84	.92
1.53	46	3.26	3.10	1.55
1.30	30	2.75	2.64	1.32
.87	4	1.76	1.73	.865
2.24	45	4.62	4.47	2.235
9.20	65	18.70	18.48	9.24
3.76	22	7.68	7.59	3.795
.46	60	1.10	.90	.45
3.15	35	6.46	6.34	3.17
1.65	50	3.45	3.27	1.635

It is possible, by direct titration in this way, to get results within .05 part chlorine per 100,000 in clear waters, when the chlorine is not higher than 10 parts. When the chlorine is low and greater accuracy is required, the water must be concentrated before titration. When this is done, there must invariably be added an excess of sodium carbonate before evaporation, as otherwise there may be a serious loss of hydrochloric acid, even if the residue is not allowed to go to dryness. Commonly 0.02 gram of sodium carbonate, or less, is sufficient, and this quantity does not in the least interfere with the titration. If too much has been used, calcium nitrate may be added before titration. An excess of nitrate does not influence the result.

I have concentrated waters in three ways, any one of which gives perfectly reliable results. First, by boiling down 500 cc. or more in a flask with sodium carbonate, to about 50 cc. By this

method there is no possibility of hydrochloric acid being absorbed from the air. It is very convenient, and gives good results when there is not too much organic matter present. In such cases the residue becomes too brown for sharp titration, and must be decolorised by aluminium hydrate and filtered.

Second, by evaporation on a water-bath with sodium carbonate, to a small bulk.

Third, by treating the solid residue of evaporation. All determinations of solids in this laboratory are made with the addition of sodium carbonate, and the ignition is made in a radiator.[1] I have found by a large number of determinations that there is no loss of chlorine whatever by igniting in this way, while all organic matter is destroyed. After the residue is weighed, the chlorides may be extracted with hot water, and transferred to a porcelain dish and titrated. When much organic matter is present, this seems to be the most accurate method, and in all cases it is very convenient. Care must be taken that no hydrochloric acid is absorbed during evaporation, and that all chlorine is washed from the residue.

The following determinations are given as illustrations of the different methods, and the correction for volume:

Serial No.	Amt. taken.	Vol. of liquid.	NaCl sol. used	$AgNO_3$ sol. required.	$AgNO_3$ corrected for vol.	Parts per 100,000.	Remarks.
		55	10	10.20	10.02		Standardisation.
2691	50	53	1 cc.	1.30	.12	.12	Direct titration.
"	500	45	0	1.53	1.38	.138	Boiled down in a flask.
"	250	20	0	.80	.72	.144	Evaporated on a water-bath.
"	250	15	0	.74	.68	.136	Solid residue.
2689	50	53	1	1.35	.17	.17	Direct titration.
"	500	50	0	1.65	1.48	.148	Boiled down in a flask.
"	250	20	0	.80	.72	.144	Evaporated on a bath.
"	200	15	0	.65	.59	.147	Solid residue.
2794	50	53	1	1.50	.32	.32	Direct titration.
"	100	15	0	.75	.68	.34	Solid residue.
2809	50	56	0	5.40	5.21	5.21	Direct titration.
"	100	30	0	10.55	10.44	5.22	Solid residue.
2821	50	58	0	7.53	7.34	7.34	Direct titration.
"	50	20	0	7.38	7.30	7.30	Solid residue.

[1] See T. M. Drown, Tech. Quarterly, Dec. '88; Chem. News **59**, 82.

No. 2691 is a sample of the city water of Lawrence; No. 2689 is a sample of city water filtered through sand; Nos. 2794 and 2809 are other clear waters, and No. 2821 is a sample of sewage.

I have made duplicate determinations of chlorine by two or more of these methods in several hundred samples of water and sewage, with exceedingly regular results, and there appears to be no source of constant error.

LAWRENCE EXPERIMENT STATION, MASS. STATE BOARD OF HEALTH.

ON ACETO-METANITROBENZOIC ANHYDRIDE.[1]

BY WILLIAM H. GREENE.

In the reaction of acetyl chloride with silver metanitrobenzoate, L. Liebermann[2] claimed to have obtained metanitrobenzoyl acetic acid, a reaction which would be inexplicable and without analogy. In the course of another investigation Bischoff and Rach[3] took the opportunity of studying the action of acetyl chloride on the silver salt of *o*-nitrobenzoic acid, and found that the reaction did not take place in the sense indicated by L. Liebermann.

Under the name acetylmetanitrobenzoic anhydride, Beilstein in his *Organische Chemie* (**2**, 786) describes the product supposed by Liebermann to be metanitrobenzoyl acetic acid, but the properties mentioned accord as little with those which this anhydride should exhibit, as with those which would be expected in the acid Liebermann thought he had obtained.

A preparation of this compound, according to the directions of Liebermann, by the addition of dry silver metanitrobenzoate to an excess of cold acetyl chloride, and pouring the product into water, yielded an acid fusing between 126° and 137°. 0.1866 gram of the silver salt of this acid yielded 0.0731 gram silver.

Ag found, 39.17 per cent. Ag calculated for nitrobenzoate, 39.42 per cent.

The acid is metanitrobenzoic, regenerated from the silver salt employed.

[1] Read at the stated meeting of the Chemical Section of the Franklin Institute, May 21, 1889.
[2] Ber. d. chem. Gesell. **10**, 863. [3] Ibid. **17**, 2799.

By the reaction of sodium metanitrobenzoate with acetyl chloride, extraction of the product with absolute ether, and evaporation of the latter, aceto-metanitrobenzoic anhydride can be readily obtained, as also by exposing silver metanitrobenzoate to the vapor of acetyl chloride and extracting with absolute ether in the same manner. It crystallises in colorless needles, fusible at 45°, and remaining fused at a much lower temperature. It is insoluble in water, by which it is not at once decomposed when crystallised, so that it may be washed with dilute sodium carbonate and water and quickly dried between filter papers without change. The presence of either alcohol or water in the ether used for extraction results in the complete decomposition of all the anhydride.

REVIEWS AND REPORTS.

AUS JUSTUS LIEBIG'S UND FRIEDRICH WÖHLER'S BRIEFWECHSEL IN DEN JAHREN 1829–1873. Unter Mitwirkung von Fräulein EMILIE WÖHLER herausgegeben von A. W. HOFMANN. Zwei Bände. Braunschweig, 1888. Vieweg.

Rarely have chemists been given such a treat as is afforded by these remarkable letters of Liebig and Wöhler. As indicated in the title, they cover a period of forty-four years, beginning in 1829, when Liebig was 26 years old and Wöhler 29, and ending in 1873, when Liebig died. It appears that the correspondence was begun in consequence of the fact that both chemists were working on certain derivatives of cyanogen. The first letter has reference to the relations between cyanuric acid and cyanic acid. Soon afterwards Wöhler suggests that they should undertake a piece of work together, he to work in Berlin and Liebig in Giessen. "Ich überlasse die Wahl des Gegenstandes ganz Ihnen," he writes. Liebig is heartily pleased by the suggestion, and proposes an investigation on the action of sulphur chloride on ammonia. Wöhler is obliged to decline this, as he dare not work with chlorine; but he suggests the desirability of working up mellithic acid, and a week later Liebig communicates the first results of his investigation. Soon afterwards they began a piece of work on cyanic acid which occupied them for some time.

In 1832 we find them working on the oil of bitter almonds, a subject suggested by Wöhler. On May 30 he writes: "Dass dir die Aufgabe Bittermandelöl gefällt, freut mich. Nun rasch daran." On July 12 again: "Ich habe vorläufig schon allerlei Versuche damit vorgenommen, ohne zu einem präcisen Resultate gekommen zu sein. Es scheint ein harter Nuss zu sein." But on August 30, after the two friends had worked together for a few weeks, Wöhler again writes: "Ich sende Dir anbei die Bittermandelöl-Abhandlung." This great research, which exerted a controlling influence on the thoughts of chemists and formed the foundation of the radical theory, was first suggested on May 30, and the work was completed and the memoir written by August 30 of the same year. In the following year (1833) the effect of this paper was already apparent to the authors. Liebig writes, March 15, 1833: "Die Pariser sind über diese Abhandlung ganz toll. Pelouze schreibt mir: 'On ne parle plus à Paris dans le monde chimique que de vos experiences. Venez donc avec M. Wöhler, venez-y recevoir le tribut d'hommages qui vous est dû.'"

Liebig's quick temper and his harsh criticisms were a constant source of anxiety to Wöhler, who made frequent though ineffectual efforts to calm his friend. A few extracts will indicate his method: "Du hast mich misverstanden. Ich habe ja nicht gemeint, dass Du Deine Ansichten, wenn sie von denen Anderer abweichen, zurückhalten sollst, das wäre ja verrückt von mir, sondern ich habe nur gewünscht, dass Du Deinen Widerspruch in eine etwas andere, minder verletzende Form einkleiden mögest. Denn gerade weil Du dies bisweilen versäumst und Deine Meinung mit derben, oft feindselig aussehenden Worten aussprichst, so kann Niemand wissen, wie eigentlich Deine persönlichen Gesinnungen für den, gegen welchen Du Dich aussprichst, beschaffen sind, ob Du ihn achtest oder verachtest, ob Du seine sonstigen Verdienste anerkennst oder als Dreck betrachtest. Lichtenberg sagt irgendwo: 'Da, wo man sonst Einem eine Ohrfeige gab, sagt man jetzt, erlauben Sie gütigst.' Es wird doch verschieden aufgenommen, ob man Jemandem sagt: Du hast eine Dummheit gemacht, Du bist ein Esel, oder ob man sagt: Ich bin anderer Meinung und glaube, die Sache verhält sich so und so."

In 1840 Liebig began to give his attention to physiology and agriculture. April 2, 1840, he writes: "Du weisst, ich schreibe soeben eine närrische Chemie, die es mit der Physiologie und dem Ackerbau zu thun hat. Was werden die Leute für Augen machen, dass ein Chemiker sich herausnimmt zu behaupten, die Physiologen und Agronomen seien die unwissendsten Pfuscher!" Soon afterwards the celebrated article "Ueber den Zustand der Chemie in Preussen" was written. In regard to this Liebig writes: "Hätte ich es mit Dir und zwei oder drei Anderen zu thun gehabt, so wäre vieles überflüssig gewesen; allein mein Zweck ist, auf das grosse Publicum und auf die Regierungen zu wirken. Der Himmel gebe seinen Segen dazu und emancipiere

uns. Die Chemie stand bisher, den anderen Fächern gegenüber, in einer sonderbaren Lage, wir werden gewissermassen als Eindringlinge betrachtet; allein dies soll sich ändern, sie soll neben oder über den anderen stehen." Liebig is now tired of laboratory work, and in 1841 he writes: "Die Lust am Laboriren verliert sich später, wir haben genug laborirt, und ich bin es ungeheuer müde. Alle diese Specialitäten interessiren mich nicht mehr, nur die Anwendungen reizen mich, und dies muss Gegenstand der späteren Lebensperiode werden." October 22, 1843, he writes again: "Ich bin jetzt in Verlegenheit über Aufgaben und Fragen zu Arbeiten und verwünsche oft das ganze Laboratorium; ich tröste mich nur, dass es Dir auch so geht." That Wöhler at times felt the same appears in several letters. Thus on January 24, 1845, he writes: "Die Schulmeisterei bin ich herzlich satt, auch das Praktikum langweilt mich *souverainement*." And again, in December of the same year: "Das verdammte Prakticum hat mich bis jetzt so sehr in Anspruch genommen, dass ich alles darüber versäume und vergesse. Lange kann man es wirklich nicht mehr aushalten, oder, was ebenso schlimm ist, man lässt die Sache ins Liederliche ausarten und muss dann sagen hören: es geht mit ihm bergab."

Liebig's investigation on creatine acquires a new interest when we read under date December 18, 1846: "Ich habe jetzt einen alten, mageren Gaul verarbeitet und hoffe so viel Kreatin zu bekommen, dass ich die Untersuchung beendigen kann." Wöhler's reply is characteristic in its humor: "Ich sehe im Geist die übelriechenden Kochereien die Du jetzt in Deinem Laboratorium vornehmen und rieche die Pferdefleischsuppen, die Du kochen lässest. Eine colossale Idee, einen ganzen Gaul zur Kreatin-Bereitung zu verwenden. Ich gratulire zu der neuen Frau Base. Das sind ja wunderbare Dinge."

Immediately after the death of Berzelius Liebig writes: "Ich bin entschlossen, mit Kopp und Andern künftig einen Jahresbericht herauszugeben, wenn auch nur deswegen, um denselben nicht in andere und schlechtere Hände fallen zu lassen."

The troubles of 1848 and 1849 led Liebig to think of a solution of the problem as far as he and Wöhler were concerned, which might have had an incalculable influence on this country. On May 29 he writes: "Wird es auf der andern Seite ebenso schlimm, und ist ein Blutbad unvermeidlich, so gehen wir Alle nach Amerika und gründen dort eine deutsche Universität."

In 1852 Liebig accepted a call to Munich, one of the conditions being that he should not be obliged to teach in the laboratory, and, further, the number of lectures he was to give was small. "Ich werde im Sommer wöchentlich nur zweimal (je 1½ St.) lesen; ich nehme Prakticanten an, die aber an mich nichts bezahlen, so dass ich in dieser Hinsicht nicht gebunden bin." Later he writes: "Ich nehme keine Eleven in mein Laboratorium auf mit der Verpflichtung, sie zu unterrichten; aber ich will einer Anzahl von

jungen Männern erlauben, in meinem Laboratorium zu arbeiten und die Hülfsmittel zu benützen, die es darbietet, ohne jedoch dass sie irgend Ansprüche wegen Aufgabe oder Leitung einer Arbeit an mich machen dürfen. So viel es mir bequem ist, werde ich mich immer mit ihnen beschäftigen, aber nicht mehr. Theurer Freund, Du wirst mich verstehen; ich habe 28 Jahre lang diesen Karren in dem Dreck gezogen, und es fehlt mir die Kraft, es ferner zu thun. Wenn ich irgend noch thätig sein will, so muss ich mich beschränken. Ich fühle, wie wohl es mir ist, dieser Qual ledig zu sein; seit Jahren war ich nicht so gesund als diesen Winter, bloss weil ich weniger meinen Kopf anzustrengen hatte. Auch bei Dir wird die Zeit kommen, und ich wünsche Dir Glück dazu, wenn Du die Gelegenheit hast Dich loszuschälen. Wir haben unser Leben lang geschafft und gearbeitet genug, Keiner, ich sage mit Wahrheit, Keiner wird es uns nachmachen."

From this time on Liebig gave but little attention to pure chemistry. Wöhler, however, though frequently complaining, continued to occupy himself in the laboratory and, as is well known, with brilliant results. In 1856 he fears that he will not be able to give practical instruction during the coming winter. Organic chemistry, which owes so much to the two masters, is rapidly growing away from them. Liebig does not profess to know much about it; and in 1859 Wöhler writes: "Morgen beginnt wieder meine Qual, das Prakticum, und morgen in acht Tagen die Vorlesung. Die organische Chemie ist jetzt wahrhaft zum Verzweifeln, es wird Einem übel, wenn man manche Abhandlung liest; dennoch hätte ich Lust, einen Griff darin zu thun; doch man muss nicht von ungelegten Eiern reden." In 1865 he writes: "Ich glaube es ist Zeit, die Chemie aufzugeben und Gärtner oder Eisenbahnschaffner zu werden." And a little later: "Lieber Freund, mir geht es wie Dir, die Laboratoriumsatmosphäre ist mir höchst zuwider, der Anblick eines Glases voll Salpetersäure macht mir fast übel; um die Details der organischen Chemie bekümmere ich mich fast gar nicht, das Meiste, was das junge Epigonengeschlecht macht, besteht doch eigentlich in der Ausfüllung der Maschen eines Stickmusters. Ich weiss dass ich übertreibe, und verkenne nicht, wohin diese zahllosen Arbeiten am Ende führen können. Das Einzige, was mir noch Befriedigung gewährt sind meine Vorlesungen, weil ich nun nach vierzigjähriger Uebung zu wissen glaube wie und was man vortragen soll."

In 1867 both were growing out of patience with the methods of instruction then in vogue in the laboratories. Liebig writes: "Diese Leute verstehen ganz gut eine organische Analyse zu machen, sonst aber verstehen sie nichts von der praktischen Chemie. In der Kunst Präparate darzustellen, sind sie in der Regel ganz ungeübt, sie haben keine Freude daran, sie halten es für Zeitverlust, da man heute alle Sachen in den chemischen Fabriken kaufen kann. Das chemische Studium wird in den

modernen Laboratorien immer einseitiger, und die Leute für die Praxis immer unbrauchbarer. An Chemikern, die eine gute Mineralanalyse machen können, ist ein solcher Mangel, dass ich mich jetzt vergeblich nach einem umgesehen habe." To this Wöhler replies: "Was Du über das moderne Studium der Chemie sagst, ist mir ganz aus der Seele geschrieben. Meinetwegen, ich lasse sie laufen; sie haben keine Freude und Lust mehr an den Dingen, sie wollen nur rechnen und formeln."

On December 31, 1871, Liebig writes as follows: "Lange werden wir uns Glückwünsche zu neuen Jahren nicht mehr senden können; aber auch wenn wir todt und längst verwest sind, werden die Bande, die uns im Leben vereinigten uns Beide in der Erinnerung der Menschen stets zusammenhalten, als ein nicht häufiges Beispiel von zwei Männern, die treu, ohne Neid und Missgunst, in demselben Gebiete rangen und stritten und stets in Freundschaft eng verbunden blieben."

Liebig's last letter to Wöhler was written April 3, 1873. He died April 18. Wöhler survived him ten years, his death having occurred September 23, 1883.

It would be an easy matter to quote many more interesting passages from the letters. Indeed there is scarcely a page in the two volumes that will not be read with interest. In closing this inadequate notice no more appropriate words can be used than those placed by Wöhler himself on the bundle containing the correspondence between him and Liebig:

> "Seh' ich die Werke der Meister an,
> So seh' ich das, was sie gethan;
> Betracht' ich meine Siebensachen,
> Seh' ich, was ich hätt' sollen machen."—GOETHE.

I. R.

INVESTIGATIONS ON THE TERPENES AND ETHEREAL OILS.

The terpenes have long been the subject of chemical investigation, but until quite recently the results have not been satisfactory. The statement is generally made that a large number of isomeric hydrocarbons of the formula $C_{10}H_{16}$ are known, but these have not been sharply characterised, and it has been a matter of doubt as to how many of the terpenes which have been described under different names are distinct chemical individuals, and the constitution even of the best-studied members of the group has not been determined with any certainty. During the last few years Professor O. Wallach, of Bonn (since called to Göttingen), has been engaged in the investigation of the terpenes and ethereal oils, and other related compounds, and he has thrown a great deal of light upon the chemistry of these compounds. It is the purpose of this paper to give a brief account of the results obtained in Professor Wallach's investigations as far as they have been described.

In the first paper,[1] which is by O. Wallach and W. Brass, an account of an investigation of worm-seed oil (*Oleum Cynæ*) is given. It is found that this oil consists essentially of an oxygen compound of the formula $C_{10}H_{18}O$, which, as it is isomeric with borneol, the authors call *cineol*. This combines with hydrochloric acid, forming the compound $(C_{10}H_{18}O)_2HCl$. When the hydrochlorate is heated, it undergoes decomposition in accordance with the following equation:

$$(C_{10}H_{18}O)_2HCl = 2H_2O + HCl + 2C_{10}H_{16}.$$

By conducting hydrochloric acid gas into worm-seed oil while heated, the hydrocarbon $C_{10}H_{16}$ is readily formed.

Hydriodic acid acts upon cineol thus:

$$C_{10}H_{18}O + 2HI = H_2O + C_{10}H_{18}I_2.$$

When bromine and cineol are brought together in the cold in petroleum ether, they unite to form the compound $C_{10}H_{18}O.Br_2$. If this is left undisturbed in a sealed tube in a cool place, it yields a crystallised compound, $C_{10}H_{16}Br_4$, which is formed also by the action of bromine on the hydrocarbon $C_{10}H_{16}$:

$$(C_{10}H_{18}O)Br_2 = H_2O + C_{10}H_{16} + Br_2;$$
$$C_{10}H_{16} + 2Br_2 = C_{10}H_{16}Br_4.$$

The tetrabromine addition-product melts at 125.5°. The authors call the hydrocarbon, $C_{10}H_{16}$, obtained from cineol, *cinene*. It is obtained most readily by heating the iodide, $C_{10}H_{18}I_2$, in aniline:

$$C_{10}H_{18}I_2 + 2C_6H_5NH_2 = C_{10}H_{16} + 2C_6H_4NH_2I.$$

Concentrated sulphuric acid converts cinene into cymene; as does also phosphorus pentasulphide.

Having found that at least one of the terpenes can be sharply characterised by chemical reactions, an investigation of terpenes in general suggests itself.[2] The first result is to show that the oxygen compound contained in cajeput oil, and hitherto known as cajeputol, is identical with cineol. It is found further that the hydrocarbon $C_{10}H_{16}$, obtained from *oleum corticis auriantorum*, and known as *hesperidene*, is not identical with cinene, as it yields a tetrabromide which melts at 104°–105°. There are then at least two distinct tetrabromides which can be obtained from terpenes, and which can be easily recognised. With this knowledge Wallach proceeds to examine a large number of ethereal oils, and the results obtained may be summed up in these words:[3]

(1). Those terpenes which are obtained from orange-peel oil, lemon oil, oil of bergamot, oil of caraway, dill oil, erigeron oil, and pine-needle oil, are identical. This hydrocarbon is the *hesperidene* above referred to. It yields a tetrabromide melting at 104°–105°, and is thus easily recognised.

(2). The terpenes boiling between 180° and 182°, and known as cinene, cajeputene, caoutchene, diisoprene; that portion of the

[1] Annalen der Chemie **225**, 991 (1884). [2] Ibid. **225**, 314. [3] Ibid. **227**, 297.

oil of camphor which boils between 180° and 182°; the product obtained by heating terpenes to 250°–270°; and finally the hydrocarbons obtained by decomposition of the terpene dichlorhydrate $C_{10}H_{16}.2HCl$, melting at 49°–50°, no matter what the source may be—all the above are identical. They yield the tetrabromide melting at 125°.

Whether all the very similar terpenes boiling at about 160°, which are found in oil of turpentine, pine-needle oil, juniper oil, lemon oil, eucalyptus oil, mace oil, dill oil, sage oil, etc., are identical or not cannot be positively stated as yet. It is, however, certain that they are all converted into the same hydrocarbon at higher temperatures.

In investigating the products formed in the destructive distillation of caoutchouc, the author readily obtained two, viz. *caoutchene* and *isoprene*. The former is unquestionably identical with cinene. Isoprene boils at 34°–39°. While heated alone it is polymerised, yielding caoutchene or cinene. It follows from this that some of the terpenes bear to the pentenes C_5H_8, the same relation that diamylene bears to amylene.

The author now proposes the following classification of the terpenes:

A. Hemiterpenes or Pentenes of the Formula C_5H_8.

Examples: Isoprene and valerylene.

B. Terpenes proper, $C_{10}H_{16}$.

These fall into several groups, each of which is composed of several members:

1. *Pinene Group.*

These boil at about 160°; give bromine addition-products which are liquid; nitroso-derivatives melt at 129°; combine with one molecule hydrochloric acid to form saturated compounds. By heat and acids they are converted into other groups.

Examples: Terebentene, australene.

2. *Camphene Group.*

These are solid; melt at about 50°, and boil at about 160°. Their conduct towards bromine is yet to be investigated.

3. *Limonene Group.*

Boiling point between 175°–177°; have characteristic odor of lemons; nitroso-derivative melts at 71°; bromine addition-product melts at 104°–105°; addition-product with hydrochloric acid (+ 2HCl) melts at 50°, and is identical with dipentene dihydrochlorate; converted into dipentene by heat.

Examples: Hesperidene, citrene, carvene. These are identical and are called *limonene*.

4. *Dipentene Group.*

Boiling point 180°–182°; odor like that of limonene; tetrabromide melts at 125°; takes up two molecules of hydrochloric acid, forming a compound which melts at 49°–50°; at high temperature undergoes polymerisation without previous conversion into another modification.

Examples: Diisoprene, cinene, cajeputene, caoutchene, isoterebentene. These are identical and are called *dipentene.*

C. POLYTERPENES, $(C_5H_8)x$.

Some of these occur ready formed in nature, while others are formed by polymerisation of hemiterpenes and terpenes. But little is known in regard to them.

1. *Sesquiterpenes or Tripentenes,* $C_{15}H_{24}$.

Boiling point 250°–260°.
Examples: Cedrene, cubebene, etc.

2. *Diterpenes or Tetrapentenes,* $C_{20}H_{32}$.

Boiling point above 300°.
Example: Colophene.

3. *Polyterpenes,* $(C_{10}H_{16})x$.

Example: Caoutchouc.

A thorough examination of Russian and Swedish oil of turpentine[1] shows that these consist essentially of pinene, sylvestrene, and dipentene, the most characteristic constituent being sylvestrene. When this is treated with hydrochloric acid in ethereal solution it yields a hydrochlorate melting at 72°. It is shown, further, that terpine hydrate is a saturated compound. When it is boiled with acids or with dehydrating agents, the first product formed is terpineol, $C_{10}H_{18}O$, and by further dehydration three different hydrocarbons are formed according to the conditions. These are *terpinene*, *terpinolene*, and *dipentene.* Terpineol is an unsaturated monatomic alcohol. Next a pure *sesquiterpene,*[2] which is found in cubeb oil, oil of patchouly, galbanum oil, and abundantly in juniper oil (*oleum cadinum*) and sabine oil (*oleum sabinæ*), is thoroughly studied.

In the fifth paper Wallach[3] states that it is now possible sharply to characterise eight hydrocarbons, $C_{10}H_{16}$, so that it is not difficult to recognise them. These are: Pinene, camphene, limonene, dipentene, terpinolene, sylvestrene, terpinene, and phellandrene.

1. *Pinene,* and 2. *Camphene.*—When cold pinene is saturated with hydrochloric acid, a compound of the formula $C_{10}H_{16}.HCl$ is formed. This can be distilled almost without decomposition.

[1] Annalen der Chemie **230**, 225 (1885). [2] Ibid. **238**, 78 (1887). [3] Ibid. **239**, 1 (1887).

It acts like a saturated compound. When the hydrochlorate is heated to 200° with sodium acetate and glacial acetic acid, it is converted into camphene. Pinene can be converted also into dipentene by heating the free hydrocarbon; by the action of moist hydrochloric acid; by the action of dilute nitric or sulphuric acid. On the other hand, dilute sulphuric acid, which so easily transforms pinene, acts very slowly upon camphene. The atoms in the molecule of camphene are apparently in a condition of more stable equilibrium than the atoms in the molecule of pinene.

3. *Limonene.*—This is strongly dextro-rotary. It forms a tetrabromide melting at 104°–105°. This also is dextro-rotary. With hydrochloric, hydrobromic, and hydriodic acids it forms compounds of the formulas $C_{10}H_{16}.2HCl$ (m. p. 50°), $C_{10}H_{16}.2HBr$ (m. p. 64°), and $C_{10}H_{16}.2HI$ (m. p. 77°–79°). These compounds are optically inactive and are derivatives of dipentene.

4. *Dipentene.*—This is formed by superheating isoprene, pinene, and limonene, and is therefore found in all those terpene oils in the preparation of which a high temperature is used, as, for example, the Russian and Swedish oils of turpentine, and in caoutchene. It is formed also by the action of sulphuric acid on pinene; by the dehydration of terpine hydrate, terpineol, and cineol; by the action of hydrochloric acid on pinene and limonene; by the action of the same acid on terpine hydrate, terpineol, and cineol. Dipentene and all its derivatives are optically inactive. Its most characteristic derivatives are the tetrabromide (m. p. 125°); the dihydrochlorate, $C_{10}H_{16}.2HCl$ (m. p. 50°); the dihydrobromate, $C_{10}H_{16}.2HBr$ (m. p. 64°); the hydriodate, $C_{10}H_{16}.2HI$ (m. p. 77°–79°). It is easily converted into terpinene by sulphuric or hydrochloric acid.

5. *Terpinolene.*—This hydrocarbon is formed by boiling terpine hydrate, terpineol, or cineol with dilute sulphuric acid, and by the inversion of pinene with sulphuric acid. Its boiling point lies between 185° and 190°. Its tetrabromide melts at 116° when perfectly pure. The solutions of the tetrabromide are optically active. It appears that terpinolene, like limonene, is converted into dipentene by treatment with the halhydric acids. Terpinolene is certainly one of the most changeable terpenes.

6. *Sylvestrene.*—This is most readily obtained from Swedish oil of turpentine. It boils at 175°–178°. When heated to 250° in sealed tubes it is partly polymerised, but apparently it is not converted into an isomeric modification. It is one of the most stable of the terpenes. It is dextro-rotary. The hydrochlorate $C_{10}H_{16}2HCl$ melts at 72°, and its solutions are dextro-rotary; the hydrobromate $C_{10}H_{16}2HBr$ also melts at 72°. The tetrabromide $C_{10}H_{16}Br_4$ melts at 135°–136°, and its solution in ether is dextro-rotary.

7. *Terpinene.*—This is obtained together with other substances by heating terpine hydrate with dilute sulphuric acid, and by the inversion of pinene with alcoholic sulphuric acid. It is formed, further, when oil of turpentine (pinene) is shaken with concentrated

sulphuric acid, if care is taken to prevent too great a rise of temperature. It is easily recognised by the aid of its nitrite $C_{10}H_{16}N_2O_3$, which is made by bringing it together with acetic acid and a water solution of sodium nitrite. The nitrite crystallises well and melts at 155°. With the halhydric acids terpinene gives only liquid products. Terpinene is not easily converted into another terpene by the action of sulphuric acid, and is one of the stable terpenes.

8. *Phellandrene.*—This hydrocarbon occurs in water fennel oil (*Phellandrium aquaticum*) and in bitter fennel oil. It was discovered by Cahours in the former and afterwards found by Pesci in the latter. It is easily recognised by the aid of its nitrite, which melts at 94°. The oils containing phellandrene are strongly dextrorotary, while the nitrite of the hydrocarbon is levo-rotary. A solution of the nitrite in chloroform does not take up bromine, its conduct being like that of a saturated compound. It is difficult to obtain phellandrene in pure condition, and it is certain that it is one of the most changeable terpenes. Treatment with hydrobromic acid in solution in glacial acetic acid converts it into dipentene. When heated for a few hours with alcoholic sulphuric acid it is converted into terpinene.

The eight modifications of terpene which are certainly known can be grouped in three classes.

A. The members of the first class combine with one molecule of hydrochloric acid, and have, therefore, but one double bond between carbon atoms.

B. The members of the second class combine with two molecules of hydrochloric acid, and have, therefore, two double bonds between carbon atoms.

C. The members of the third class are distinguished by their power to form addition-products with nitrogen trioxide. These compounds are formed in cases in which an aromatic substance contains an unsaturated paraffin residue.

The terpenes of the first class (A) are pinene and camphene.

Those of the second class (B) are limonene, dipentene, sylvestrene, and terpinolene.

Those of the third class (C) are phellandrene and terpinene.

The easy formation of the addition-products with nitrogen trioxide leads next to a more careful study of the reaction involved, and the results obtained are described in four papers. These results will be presented in a connected way below, as some of them are only indirectly related to the chief problem under discussion.

The next paper[1] bearing upon the relations between the terpenes is the eighth in the series. This is of special importance. The author's latest investigations have shown that the pine-needle oils contain limonene, but not the ordinary variety. Ordinary limonene is dextro-rotary, while that contained in the pine-needle oils is levo-rotary. The tetrabromide melts at 104°, as does that from

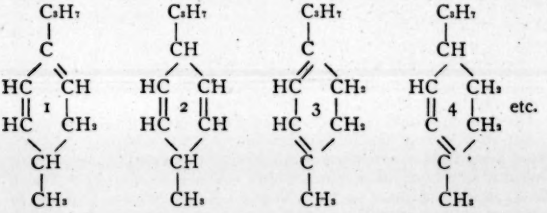
[1] Annalen der Chemie **246**, 291 (1888).

ordinary dextro-limonene. It crystallises in the same forms with the same angles, *but with opposite hemihedral faces.* The solution of the tetrabromide of levo-limonene is levo-rotary, and the solution of the tetrabromide of dextro-limonene is dextro-rotary. It appears, therefore, that dextro-limonene and levo-limonene are chemically identical, but physically isomeric hydrocarbons. Of great interest is the fact that *when the dextro- and levo-limonenes are mixed in equal quantities, dipentene is formed.* When such a mixture is treated with bromine, the tetrabromide, melting at 124°–125°, is formed, whereas each of the limonenes gives the bromide melting at 104°–105°. Further, when the dextro-rotary tetrabromide and the levo-rotary tetrabromide are mixed, the tetrabromide melting at 124°–125° is formed.

The above relations are strongly suggestive of those which exist between dextro- and levo-tartaric acids and racemic acid.

Just as two varieties of limonene have been found, so the author has also found two varieties of phellandrene. That variety which occurs in elemi oil is dextro-rotary, while that which occurs in eucalyptus oil is levo-rotary. The nitrite of dextro-phellandrene is levo-rotary, and that of levo-phellandrene is dextro-rotary. When the two active nitrites are mixed together, an inactive nitrite is formed. It has not yet been determined what hydrocarbon is formed by mixing dextro- and levo-phellandrene.

It is an easy matter to devise structural formulas which will account for the facts thus far established. It appears that some of the terpenes, those which take up two molecules of hydrochloric acid, and therefore probably have two double carbon bonds, are true hydrocymenes. For these a large number of formulas are possible according to the theory. The following may serve as examples:



A compound of formula 1 should be optically active; one of formula 2 inactive. The same would be true of their bromine addition-products, while it is clear that two molecules of hydrochloric acid could be added to 1 and to 2 in such ways as to give identical inactive compounds. The author, however, wisely restrains from premature speculation on the subject, as he is convinced that the facts known are not sufficient to justify a conclusion in regard to the constitution of any one of the terpenes.

In the eleventh paper in the series[1] some new relations between the derivatives of dipentene are discussed. It has already been shown that when dextro-limonene and levo-limonene are mixed, dipentene is formed. The relations between the two optically active varieties of limonene and inactive dipentene are like those between dextro- and levo-tartaric acids and racemic acid. But, as is well known, there is an inactive tartaric acid, and the question will suggest itself whether there is a second variety of dipentene. Investigation shows that there is. Levo-limonene was converted into the nitroso-chloride, when it was found that the product consisted of two isomeric varieties (α- and β-), both of which are levo-rotary. So also dextro-limonene yields two isomeric nitroso-chlorides (α- and β-) both of which are dextro-rotary. When these nitroso-chlorides are treated with bases, as aniline, piperidine, etc., each one gives a different base with the same optical activity as the nitroso-chloride from which it is formed. Thus:

$+$ Limonene gives $+$ α-Base and $+$ β-Base;
$-$ Limonene gives $-$ α-Base and $-$ β-Base.

Further, when $+$ α-Base and $-$ α-Base are mixed, they give a new base which is inactive; and $+$ β-Base and $-$ β-Base also give a new base which is inactive. These two new bases are derivatives of dipentene, and a mixture of the two is obtained when dipentene is taken as the starting point. The relations existing between these various compounds is shown by the table below:

$+$ Limonene and $-$ Limonene give Dipentene.
$+$ Limonene yields { (1) $+$ α-Base. (2) $+$ β-Base.
$-$ Limonene yields { (3) $-$ α-Base. (4) $-$ β-Base.
$+$ α-Base and $-$ α-Base give (5) α-Base (inactive).
$+$ β-Base and $-$ β-Base give (6) β-Base (inactive).

Dipentene yields α-Base (inactive) and β-Base (inactive). Starting with dipentene, therefore, it is possible theoretically to obtain through the nitroso-chloride six different bases.

On the Nitrosates and Nitrosites.—As it has been shown that some of the terpenes have the power to combine with oxides of nitrogen, while others have not, and that this power is clearly connected with the presence of unsaturated paraffin residues, an investigation of some of the compounds thus formed is taken up. In a paper[2] entitled "Ueber Nitrosate und Nitrosite sowie über einige aus denselben darstellbare neue Verbindungen," the chief results described are as follows: The addition of the trioxide N_2O_3, and of the tetroxide of nitrogen, N_2O_4, does not always take place in the same way. The differences appear to be due for the most part to the structure of the compounds used. The compound formed by the addition of nitrogen tetroxide to amylene

[1] Annalen der Chemie **252**, 106 (1889). [2] Ibid. **241**, 288 (1887).

may serve as the representative of a large group of compounds. This substance is not a nitro-compound nor a dinitrite, $C_5H_{10}(NO_2)_2$, but it contains a nitrate group, $-O(NO_2)$, and a nitroso or isonitroso group, so that it may properly be called a *nitrosonitrate* or, better, a *nitrosate*. Some compounds formed by the addition of nitrogen trioxide to hydrocarbons are perfectly analogous to the nitrosates, but they contain a nitrite group, $-O(NO)$, instead of the nitrate group, and they may therefore be called *nitrosonitrites* or *nitrosites*. Both the nitrosates and the nitrosites undergo chemical change very readily, exchanging the nitrate or the nitrite group for other constituents with the greatest ease. With bases products are formed which contain the group NH_2, NHR or NR_2. These the author calls *nitrolamines*. Assuming that the nitrosate contains the isonitroso group, the change with aniline is represented thus:

$$C_5H_9\begin{cases}=NOH\\ ONO_2\end{cases} + H_2NC_6H_5 = C_5H_9\begin{cases}=NOH\\ NHC_6H_5\end{cases} + HNO_3.$$

Amylene-nitrosate. Nitrolanilide.

When the hydrochloric acid compound of the anilide is boiled with water or concentrated hydrochloric acid, the isonitroso group is replaced by oxygen, hydroxylamine being formed at the same time, as in the case of the acetoximes and ketoximes:

$$C_5H_9\begin{cases}=NOH\\ NHC_6H_5\end{cases} + H_2O = C_5H_9\begin{cases}=O\\ NHC_6H_5\end{cases} + NH_2OH.$$

The nitrosates act also upon potassium cyanide as represented in this equation:

$$C_5H_9\begin{cases}=NOH\\ O(NO_2)\end{cases} + KCN = C_5H_9\begin{cases}=NOH\\ CN\end{cases} + KNO_2.$$

Nitrosites of the formula $R\begin{cases}NOH\\ ONO\end{cases}$ exist. With a mixture of nitrogen trioxide and the tetroxide, sometimes a nitrosate is formed and sometimes a nitrosite, according to the properties of the product.

In a later paper[1] an account is given of a nitrosite obtained from terpinene which must be represented by the formula

$$C_{10}H_{16}\begin{cases}NO\\ O(NO)\end{cases} \text{ or } C_{10}H_{15}\begin{cases}=NOH\\ O(NO)\end{cases}.$$

According to observations made by Maissen and confirmed by Wallach, limonene yields a nitrosate. According to the above, it is probable that some of the terpenes contain unsaturated paraffin residues. Finally, a still later paper[2] in the series treats more in detail of amylene nitrosate and compounds derived from it. The object of the investigation is to determine from which amylene the nitrosate is derived. It is certain that not all unsaturated hydro-

[1] Annalen der Chemie **241**, 315 (1887). [2] Ibid. **248**, 161 (1888).

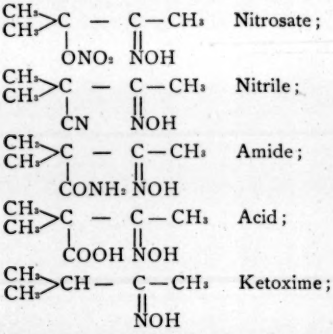
carbons yield nitrosates. Caprylene, for example, does not yield one, and the different amylenes conduct themselves differently towards the oxides of nitrogen. Amylene nitrosate is easily obtained from commercial amylene, boiling at 36°–38°. The nitrosate was first treated with potassium cyanide, and a nitrile thus formed:

$$C_5H_{10}.NO.NO_2 + KCN = KNO_2 + C_5H_{10}.NO.CN.$$

When the nitrile is boiled with caustic potash it yields colorless needles,

$$C_5H_{10}NO.CN + H_2O = C_5H_{10}.NO.CONH_2,$$

and the potassium salt of an acid of the formula $C_5H_{10}NO.COOH$ is formed at the same time. When heated above its melting point this acid loses carbon dioxide, and a liquid of the composition $C_5H_{11}NO$ is formed. This is the hydroxylamine derivative of methyl-isopropyl ketone, as was proved by making the compound directly from the ketone. The relations between the compounds mentioned are shown by the following formulas:



The acid obtained from amylene by the method described is the hydroxylamine derivative of dimethylacetoacetic acid, as appears from the following formulas:

$$CH_3-CO-C(CH_3)_2-COOH;$$

Dimethylacetoacetic acid.

$$CH_3-C(=NOH)-C(CH_3)_2-COOH.$$

The author proposes to call all acids which contain the group $-C(NOH)-CH_3$ *ketoxime acids.* Hence, the above acid is called *ketoxime-dimethylacetoacetic acid.*

The amylene used in these experiments may be either trimethylethylene, $(H_3C)_2C=CH(CH_3)$, or isopropylethylene, $(H_3C)_2CH-CH=CH_2$. If, however, it could be conclusively shown that the ketoxime acid obtained is ketoxime-dimethylacetoacetic acid, the proof that amylene is trimethylethylene would be complete. This was shown by making ethyl dimethylacetoacetate, saponifying, and treating with hydroxylamine, when the same acid was obtained as that above described. From this it follows that the amylene from which the nitrosate is derived is trimethylethylene. It appears probable, from the evidence thus far obtained, that nitrosates can be obtained from those unsaturated hydrocarbons which are trisubstitution products of ethylene. It remains to be determined how the disubstituted ethylenes $R_2C=CH_2$ and $RHC=CHR$ will conduct themselves.

The investigation on the terpenes is still in progress.

I. R.

GESCHICHTE DER CHEMIE VON DEN ÄLTESTEN ZEITEN BIS ZUR GEGENWART. ZUGLEICH EINFÜHRUNG IN DAS STUDIUM DER CHEMIE. Von Dr. ERNST VON MEYER, a. o. Professor an der Universität Leipzig. Leipzig: Veit & Comp., 1889. 466 pp. 8vo.

The author of this book has endeavored to furnish a *short* history of the development of chemical knowledge from the beginning to the present day. His work differs, therefore, markedly from Kopp's *Geschichte*, which is not short, and from Ladenburg's *Entwickelungsgeschichte*, which begins with Lavoisier. The book is clearly written, and it is evident that the author has to a considerable extent formed his own judgment in regard to the important movements. As regards the older periods, the treatment is in the main in accordance with that of other historians. Indeed, writers generally have relied upon Kopp for the early history of chemistry, and one scarcely looks for novelty of treatment in this part of the subject. For the majority of students who want to get a general idea concerning the early history of chemistry the book is well adapted.

In dealing with the work of Lavoisier the author plainly shows that his mental equilibrium has been somewhat disturbed by Würtz's unfortunate, famous phrase: "La chimie est une science française; elle fut constituée par Lavoisier," etc. He agrees with Volhard that Lavoisier was rather a physicist than a chemist, while at the same time he acknowledges the great influence of this remarkable man. He says (p. 129): "Die grosse That Lavoisier's bestand in der Abstreifung alter Vorurteile und in der mustergültigen Anwendung wissenschaftlicher Prinzipien bei der Erklärung chemischer Vorgänge. Ein reiches Material von wichtigen Thatsachen war ihm von den Phlogistikern überliefert; er selbst hat dieses durch neue Beobachtungen, was die *chemische*

Seite derselben anlangt, um wenig bereichert, wohl aber dasselbe von einem bis dahin unerreichten Standpunkte aus zu sichten und zusammenzufassen vermocht, sowie für viele Vorgänge die richtige Erklärung gegeben. Man wird nicht fehlgehen, wenn man solche Leistungen auf Rechnung seines physikalisch und mathematisch vorzüglich geschulten Geistes setzt, welcher schon frühzeitig von den Fesseln der phlogistischen Hypothese frei zu machen wusste. Als *Physiker* musste sich Lavoisier vor allen Dingen Rechenschaft geben von Gewichtsveränderungen, z. B. bei der Verkalkung von Metallen; die Eigenschaften der Produkte interessierten ihn weniger. Daraus erklärt es sich, dass er selbständige *chemische* Entdeckungen nicht gemacht hat; sein Verdienst, die Beobachtungen anderer zuerst umfassend und richtig gedeutet zu haben, bleibt darum unbestritten." It is a little difficult to understand the distinction made by Volhard and Von Meyer. It would seem that one who by the aid of his own experiments furnishes an entirely satisfactory explanation of all the phenomena of combustion must be familiar with a large number of chemical facts, must be able to grasp the great problems of chemistry, must be able to think chemically, must in short be a chemist. It matters little, however, what he is called. If the discussion is of any value, it is for the reason that it furnishes an admonition to chemists to study physics. Avogadro and Dalton were fortunately not chemists in the usual sense of the word. "Selbständige chemische Entdeckungen" are not the only things of importance for chemistry.

The influence of the researches of Würtz, Hofmann, and Williamson on the development of the theory of types is discussed very satisfactorily, so that the reader can see clearly how these researches must have worked on the minds of cotemporaneous chemists. Unquestionably the work on the substituted ammonias was of the highest importance in impressing upon chemists the reality of the view according to which these compounds are derived from ammonia by the substitution of one, two, or three of the hydrogen atoms by radicals. It was these experiments which enabled chemists to decide in favor of the typical view as against the view that the compounds are "*copulated*." There is especially one experiment of Hofmann which is almost crucial. As this, so far as the writer of this notice is aware, is not given its full due in works on the history of chemistry, a few words regarding it will not be out of place here. The question under discussion was simply this: In an ammonia-base, like aniline, is ammonia present as such, copulated with a radical as represented in the formula $C_6H_4 \supset NH_3$, or is one of the hydrogen atoms of the ammonia replaced by a radical as represented in the formula $C_6H_5.NH_2$? The former was the view commonly held in accordance with the theory of copulated compounds; the latter view had been put forward by Liebig, and was known as the amide theory. In working on the derivatives of aniline, Hofmann showed that the conduct

of aniline oxalate, under the influence of dehydrating agents, can be accounted for only by the aid of the amide theory. As is well known, when ammonium oxalate is dehydrated, two stages are observed. These are represented by the equations

$$\begin{matrix}\mathrm{COONH_4}\\ |\\ \mathrm{COONH_4}\end{matrix} = \begin{matrix}\mathrm{CONH_2}\\ |\\ \mathrm{CONH_2}\end{matrix} + \begin{matrix}\mathrm{H_2O}\\ \\ \mathrm{H_2O}\end{matrix}\text{; and}$$

$$\begin{matrix}\mathrm{CONH_2}\\ |\\ \mathrm{CONH_2}\end{matrix} = \begin{matrix}\mathrm{CN}\\ |\\ \mathrm{CN}\end{matrix} + \begin{matrix}\mathrm{H_2O}\\ \\ \mathrm{H_2O}\end{matrix}.$$

Now, if aniline is a copulated compound and contains ammonia, then aniline oxalate ought to undergo two similar changes:

$$\begin{matrix}\mathrm{COONH_4}\supset\mathrm{C_6H_4}\\ |\\ \mathrm{COONH_4}\supset\mathrm{C_6H_4}\end{matrix} = \begin{matrix}\mathrm{CONH_2}\supset\mathrm{C_6H_4}\\ |\\ \mathrm{CONH_2}\supset\mathrm{C_6H_4}\end{matrix} + \begin{matrix}\mathrm{H_2O}\\ \\ \mathrm{H_2O}\end{matrix};$$

$$\begin{matrix}\mathrm{CONH_2}\supset\mathrm{C_6H_4}\\ |\\ \mathrm{CONH_2}\supset\mathrm{C_6H_4}\end{matrix} = \begin{matrix}\mathrm{CN}\supset\mathrm{C_6H_4}\\ |\\ \mathrm{CN}\supset\mathrm{C_6H_4}\end{matrix} + \begin{matrix}\mathrm{H_2O}\\ \\ \mathrm{H_2O}\end{matrix}.$$

But the second change cannot be effected. It therefore appears improbable that ammonia, as such, is present in aniline. If, on the other hand, it is assumed that aniline is a substituted ammonia, the fact that the second change of the oxalate cannot be effected is easily understood. The following equation expresses the first change:

$$\begin{matrix}\mathrm{COONH_3.C_6H_5}\\ |\\ \mathrm{COONH_3.C_6H_5}\end{matrix} = \begin{matrix}\mathrm{CONH.C_6H_5}\\ |\\ \mathrm{CONH.C_6H_5}\end{matrix} + \begin{matrix}\mathrm{H_2O}\\ \\ \mathrm{H_2O}\end{matrix}.$$

And it will be seen that the second change cannot take place without involving the hydrogen atoms of the radical. As the above facts lead to the amide theory, so the subsequent preparation of a number of the ammonia-bases from ammonia and halogen compounds of the alkyls "konnte als ein trefflicher Beweis für die Richtigkeit der Annahme gelten, dass diese Körper aus Ammoniak durch Austausch eines oder mehrerer Wasserstoffatome gegen Alkoholradikale hervorgegangen sein" (p. 240).

Due credit is given Sterry Hunt for his part in the development of the theory of types. On p. 243 we find this passage: "Eine grössere Ausdehnung gab dieser typischen Auffassung seit dem Jahre 1848 der amerikanische Chemiker Sterry Hunt, welcher in mehreren Abhandlungen die Ableitung zahlreicher sauerstoffhaltiger Körper, unorganischer sowie organischer, von dem Wasser, die der Kohlenwasserstoffe von dem Typus Wasserstoff lehrte. Da seine Erörterungen in Europa kaum bekannt wurden, so haben dieselben auch keinerlei beschleunigenden Einfluss auf die Ent-

wickelung der ähnlichen in manchen Köpfen vorhandenen Anschauungsweise ausgeübt."

In the passage from the type theory to the valence hypothesis the chief credit is justly given to Frankland, though the influence of Kolbe is by no means forgotten. Concerning these two chemists and their work the author says (p. 259): "Diese beiden Männer, die originellsten Forscher auf dem Gebiete der organischen Chemie in jener Sturm- und Drangperiode der fünfziger Jahre, haben durch ihr Wirken ganz wesentlich dazu beigetragen, dass die Eigentümlichkeit der Gerhardt'schen Typen als beruhend auf der verschiedenen Sättigungskapazität der in denselben enthaltenen Grundstoffe erkannt wurde. Das Hauptverdienst in dieser Richtung gewirkt zu haben, fällt Frankland zu." In order that full justice may be done, a section of the book bears the title, "Begründung der Lehre von der Sättigungskapazität der Grundstoffe durch Frankland."

In discussing Kekulé's memoir, "Ueber die Konstitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs," the author says (p. 266): "Der Gedankengang ist fast der gleiche, welchen Frankland zur Ableitung der Drei- und Fünfwertigkeit des Stickstoffs, Phosphors, Arsens und Antimons führte. . . . . Daraus ergiebt sich aber, dass in jenem Ausspruch Kekulé's nicht eine durchaus originelle Leistung oder eine wissenschaftliche That erblickt werden kann, umsoweniger, als die Vierwertigkeit des Kohlenstoffs sowohl von Frankland, wie von Kolbe schon erkannt war, und namentlich den Erörterungen des letzteren über die Konstitution organischer Verbindungen zu Grunde lag. . . . Kekulé's Verdienst in dieser Angelegenheit muss darin gesucht werden, dass er der Frage nach der Art, wie sich zwei und mehr Kohlenstoffatome mit einander verbinden und ihre Affinitäten sättigen auf den Grund zu gehen suchte. Das unmittelbare Ergebnis dieser Spekulationen ist die Lehre von der Verkettung der Atome in den chemischen Verbindungen gewesen. Mittelbar haben die Ansichten Kolbe's und Frankland's an der Entwickelung dieser in der Strukturtheorie gipfelnden Betrachtungsweise den wesentlichsten Antheil gehabt."

It appears clear that chemists generally have erred in ascribing the valence hypothesis solely to Kekulé. Kekulé himself, in his memoir, says that the views put forward by him are not his own, but that they are applications of views previously expressed by others. At the same time it would not be just to fly to the other extreme, as Von Meyer seems inclined to do. While it cannot be denied that Frankland first clearly recognised the saturating power of the elements and that his work on this subject had the highest value, it must also be acknowledged that Kekulé's work exerted a powerful influence in leading chemists to recognise the truth of the new conception.

The last part of the book (pp. 300–449) has the title: "Spezielle Geschichte einzelner Theile der Chemie seit Lavoisier bis auf die

Gegenwart." The subjects treated under this general head are as follows: Geschichte der analytischen Chemie; Spezielle Geschichte der unorganischen Chemie; Specielle Geschichte der organischen Chemie im 19. Jahrhunderte; Geschichte der physikalischen Chemie in der neueren Zeit; Zur Geschichte der mineralogischen Chemie während der letzten hundert Jahre; Entwickelung der Agrikulturchemie und der physiologischen Chemie; Geschichte der technischen Chemie in den letzten hundert Jahren; Zur Entwickelung des chemischen Unterrichts im 19. Jahrhundert, namentlich in Deutschland.

The section on physical chemistry gives, in the space of twenty-seven pages, a clear account of the recent developments of this subject.

One word in regard to the title of the book. The words "Zugleich Einführung in das Studium der Chemie" are misleading. Nothing is more certain than that the history of chemistry is entirely meaningless to one who has not studied chemistry pretty thoroughly. Only the mature chemist, who by long study has become familiar with chemical changes and chemical substances, can profit by the study of the history of the science. For such a one the study is of great value and, indeed, essential if he is to understand the present views and to estimate their value fairly. As a guide to the study, Professor Von Meyer's book can be cordially recommended to advanced students. As far as possible, the original articles which are referred to should also be studied with care. Of course, in the time at the disposal of a student, only a comparatively small number of these classical articles can be thoroughly studied, but a beginning can at least be made, and a clear understanding of one brief period will be of great assistance in enabling the student to understand the whole subject. Then, too, it is well to bear in mind that the most profitable study is that which is done after the so-called student-years are over.

I. R.

FORTSCHRITTE DER THEERFARBENFABRIKATION UND VERWANDTER INDUSTRIEZWEIGE 1877–1887. AN DER HAND DER SYSTEMATISCH GEORDNETEN UND MIT KRITISCHEN ANMERKUNGEN VERSEHENEN DEUTSCHEN REICHS-PATENTE. Dargestellt von Dr. P. FRIEDLÄNDER, Privatdocent an der technischen Hochschule zu Karlsruhe i. B. Berlin: Springer. 1888.

Those who are interested in the manufacture of coal-tar dyes will welcome this book; and even scientific chemists who have no connection with patents will find much to interest them in it, for in the laboratories of the dye-factories, observations are constantly made, and most of these are lost to the outside chemical world. The author has had several years' experience on the technical side, and is thus able to give a great deal of information not usually given in books on this subject, and in cases in which his

own observations were not sufficient he has called in the aid of others. The results of his labors are given in a book of 614 pages 4to. No attempt can be made to review the book as a whole, but some idea of its extent may be gained by the statement that 94 pages are devoted to tri-phenylmethane dyes; 31 pages to indigo-blue, isatin, and indol derivatives; 71 pages to quinoline, quinoxaline, phenylpyrazol, and pyrrol compounds; and 214 pages to azo-dyes.

In the chapter on indigo we learn that of all the patents taken out bearing upon the artificial preparation of indigo, only two have any industrial importance. These are (1) that for the preparation of *o*-nitrophenyl-propiolic acid; and (2) that covering the fixing of indigo on the fiber by means of *o*-nitrophenyl-propiolic acid and xanthogenates. But the demand for the acid remains very small. Of the large number of quinoline derivatives, methods for the preparation of which have been patented, only three are of importance from a technical point of view. These are quinaldine, thalline, and kairine. The members of the pyrazol group, which are made by the action of primary hydrazines with β-diketo compounds, are of importance on account of their physiological action. As is well known, that one which is most extensively used is antipyrine.

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